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Origin and Chemical Composition of Androscoggin River Foam

Edward C. Jordan Co., Inc.
Portland, ME

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ORIGIN AND CHEMICAL COMPOSITION OF ANDROSCOGGIN RIVER FOAM

by

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E.C. Jordan Co.
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Contract Number 68-03-2605
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FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory - Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

This report provides useful information concerning the original and chemical composition of Androscoggin River foam. The report forms a solid basis for further studies into the origin and chemical composition of river foam and eventual recommendations for elimination or reduction of the foaming condition. Regulatory agencies can use the information to formulate plans for further study. The Food and Wood Products Branch, IERL-Cincinnati, Ohio, can be contacted for further information on the subject.

David G. Stephan, Director
Industrial Environmental Research Laboratory
Cincinnati, OH

ABSTRACT

A sampling and analysis program on the Androscoggin River and at International Paper Company's Androscoggin Mill in Jay, Maine was undertaken to determine the origin and chemical composition of Androscoggin River foam. The report documents an extremely complex chemical composition of river foam. A mass balance of downstream river foam accounts for approximately 50 percent of both organic and inorganic matter. River samples downstream of both industrial and municipal point sources foamed, but locations upstream of any point sources foamed as well. It could not be determined from the data generated in this study whether any of the industrial or municipal point sources acted alone, or in combination with one another and/or ambient conditions to cause the foaming condition.

This report was submitted in fulfillment of Contract No. 68-03-2605, Work Directives Nos. 2, Part II, and 7 by the E. C. Jordan Co., under the sponsorship of the U.S. Environmental Protection Agency. This report covers the period May 4, 1978 to September 10, 1980, and work was completed as of June 25, 1980.

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LIST OF ABBREVIATIONS AND SYMBOLS

ABBREVIATIONS

BOD --biochemical oxygen demand
BOD_5 --5-day biochemical oxygen demand
BP --bleach plant acid sewer
BS --brownstock washer effluent
DEP --State of Maine Department of Environmental Protection
COD --chemical oxygen demand
DBS --dodecylbenzene sulfonate
DI --de-ionized
ECD --electron capture detection
FE --final effluent from the secondary clarifier
EPA --U.S. Environmental Protection Agency
FID --flame ionization detector
ft --feet (foot)
ft^2 --square feet
ft^3 --cubic feet
g --gram
gal --gallon
GC --gas chromatography
GC/MS --gas chromatography/mass spectrometry
gpd --gallons per day
gpm --gallons per minute
GSRI --Gulf South Research Institute
hp --horsepower
HPLC --high pressure liquid chromatography
in --inches
IP --Interational Paper Company
kg --kilogram
kW --kilowatt
kWh --kilowatt-hour
l --liter
lb --pound
M --molar
MBAS --methylene blue active substances
m/e --mass/charge
min --minute
mg --milligram
mg/l --milligram/liter
ml --milliliter
ml/l --milliliter/liter
MLSS --mixed liquor suspended solids

ABBREVIATIONS (Continued)

MLVSS --mixed liquor volatile suspended solids
MSTFA --N-methyl-N-trimethylsilyl trifluoroacetamide
N --normality
O&M --operation and maintenance
ppb --parts per billion
ppm --parts per million
POTW --publicly owned treatment works
sec --seconds
ug/l --micrograms per liter
umhos --micromhos
w --watt(s)
wt --weight

SYMBOLS

°C	degrees Celsius
CH_2Cl_2	dichloromethane
°F	degrees Fahrenheit
HCl	hydrochloric acid
H_2SO_4	sulfuric acid
H_2O	water
NaOH	sodium hydroxide
>	greater than
<	less than
%	percent

DEFINITION OF TERMS

Fatty acids	--straight-chain mon-carboxylic acids derived from the hydrolysis fats
Resin acids	--the carboxylic acid substituted partially reduced phenanthrene nucleii family of compounds found in the ether soluble portion of wood
Chloroguaiacols	--3,4,5-trichloro and tetrachloro-o-methoxyphenols
MBAS	--methylene blue active substance
Polyaromatic pulping products	--the substances found in the pulping process that absorb light in the region of 254 nm and elute at retention times between 1.0 and 1.7 minutes in HPLC under the conditions described in Appendix A
Pristine foam	--derived from a reach of river that is still pure or untouched

ACKNOWLEDGEMENTS

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Special acknowledgement is given to the Maine DEP for performing the ambient phases of the study. We appreciate the supervision by Gardner S. Hunt and the technical input and analytical efforts by Jack Krueger.

Appreciation is extended to Dr. Daniel W. Armstrong for his technical consultation, HPLC methods development, analysis of strongly acidic surfactants in Phase III and IV samples.

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Station 17

August 21, 1980

Mr. William Warren
E.C. Jordan Co.
P.O. Box 7050
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Portland, Maine 04112

Dear Bill:

Bruce Wallin has asked me to respond to several minor questions you have raised regarding my report to you dated March 28, 1980 on Foam in the Androscoggin River. I will address each item as follows:

1. Item: page 3 (blender use)
   Response: The DEP's blender test is the method described by ASTM # D3519-76, the same used by E.C. Jordan. We modified the method slightly by extending the blender time until measurable foam was generated. That time interval (3 minutes) was applied to all samples in order to determine relative foamability among samples. Since it is merely a comparison of foamability within a set of samples, the blender time interval is common to all samples and has no impact on the comparison within the set.

2. Item: page 6 (modified Total Kjeldahl Nitrogen)
   Response: The EPA method for TKN has been adapted to automation by documented Technicon Autoanalyzer methodologies. Although the automated methodology is not officially adopted by EPA, we find it suitable for dissolved and water transportable solids. The method has been used for several years and its viability document by rigorous quality control.

3. Item: Methylation method
   Response: The diazomethane method of methylation is identical to the one used by E.C. Jordan. Results should be directly comparable.

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4. Item: Margaric Acid as an internal standard
   Response: Margaric acid is also known as heptadecanoic acid. The material is used as an internal standard to compare intersample retention time and instrument response for GC analysis. Its choice is predicated upon its absense in the environment and is also used as by E.C. Jordan for the same purpose.

5. Item: change to capillary columns
   Response: Capillary columns used in GC analysis are vastly superior in resolution to the older packed columns. We switched in order to do the best analytical job possible and minimize the co-elution problems which are ever present, especially with packed columns. Results should be comparable.

This should answer your questions. If you have more, please advise.

Yours truly,

Gardner S. Hunt
krs
Gardner S. Hunt
Director, Division of Laboratory and Field Services

GSH/krs

cc: Bruce Wallin, E.C. Jordan

S-2

SECTION 1
INTRODUCTION

BACKGROUND

For some time the rivers of northern New England have been known to be prone to foaming. Foaming on rivers in other areas of the country is less well documented, though there are examples of estuarine foam problems such as Peridido Bay in Florida (1).

Foam is defined as a dispersion of gas bubbles in a liquid. In order for foam to occur, a critical concentration of a surface active substance must be present. Surface active substances or surfactants are described as molecules having both hydrophilic and hydrophobic groups. The hydrophilic group has a tendency to unite with water, and the hydrophobic group is not capable of uniting with water. This property causes surfactants to concentrate at the gas/liquid interface, thus satisfying both portions of the molecules, and under proper conditions foam is formed.

For many years the State of Maine Department of Environmental Protection (DEP) has received public comments voicing concern about accumulations of foam on the Androscoggin River. Generally, the public has perceived foam as an aesthetic problem introduced to the river by the several pulp, paper, and paperboard mills located on the river. However, sources of surfactants include publicly owned treatment works (POTW) and nonpoint sources, as well as the pulp, paper, and paperboard industry.

Foaming has been an historical problem within pulp, paper, and paperboard mills. Resin and fatty acids were identified years ago in their effluent. Resin and fatty acids are structurally surface active. The concentration it takes to make them surface active (and cause foam) is variable with different compounds and classes of compounds, but the fact remains that resin and fatty acids are surface active.

Publicly owned treatment works (POTW) may also be a source of surfactants. If a POTW treats purely municipal wastes (no industrial contributions), there are two general categories of surfactant contributors - manmade detergents, the sulfonates and neutrals; and surfactants that result from biological treatment itself. The metabolic breakdown of the biological treatment process results in the release of fatty acids, and human fecal matter contains fatty acids that are the result of incomplete absorption of the human digestive tract.

Nonpoint sources may also contribute to foaming potential in the river. Agricultural lands may contribute fatty acids from fecal matter on pasture lands. Rural forest lands may also contribute fatty acids from decaying biological materials. Protein, which is a product of any biological process, is somewhat surface active, but it would not be expected to be found naturally in any appreciable quantities in a stream or river.

The Androscoggin River headwaters are in northwest Maine, where it flows eastward from Umbagog Lake through Errol and Berlin, New Hampshire, then back into Maine through the towns of Rumford, Jay, Lewiston, and Brunswick, before discharging to the Atlantic Ocean at Merrymeeting Bay. Three bleached kraft mills and one groundwood mill are located along the Androscoggin's 200-mile length: Brown Company in Berlin, New Hampshire; Boise Cascade Corporation in Rumford, Maine; International Paper Company in Jay, Maine, and Pejepscot Paper Company in Topsham, Maine. Each of the three bleached kraft mills produces pulp at a rate of approximately 1,000 tons per day (tpd), the groundwood mill at a rate of 150 tons per day, and each is served by a secondary wastewater treatment facility.

STUDY OBJECTIVES

Several organizations worked together on the evaluation of Androscoggin River foam. An explanation of how the project unfolded puts the roles of the participants in perspective. First, the public voiced concerns to the State of Maine DEP over foam accumulations on the Androscoggin River. DEP requested assistance from the EPA when the problem was found to be beyond the state's funding and technological capabilities. Since the E. C. Jordan Co. was under contract with EPA, it was retained to study the problem. The DEP was to provide support by performing an ambient sampling and analysis program on the Androscoggin River. Battelle Laboratories was contracted by EPA to assist in the study by elucidation of the Androscoggin River foam. It was felt that the ultimate success of the project depended on a detailed chemical breakdown of the most complex foam, the terminal foam. Daniel W. Armstrong, Ph.D., was subcontracted by E. C. Jordan Co. after some of Battelle's early analyses had begun to uncover the extreme complexity of the foam chemistry. Dr. Armstrong is a chemist who specializes in surface active material and, therefore, his role in the project was to help with some of the problems of surfactant chemistry.

At the outset of this study, the objectives were defined as follows:

1. Definition of the chemical constituents causing both naturally occurring foams and foams associated with pulp, paper, and paperboard mill discharges.
2. Development, through laboratory and pilot plant studies, of foam removal and treatment technologies capable of yielding non-foam generating mill effluents; and
3. Assessment of the effectiveness of the developed removal and treatment technologies for minimizing and/or eliminating surfactants in mill's final effluent.

Due to the lack of available literature and in-place technology to solve the foam problem, these objectives outlined an ambitious program. During the initial phases of this study, the objectives were redefined as follows:

1. Determine the chemical composition of Androscoggin River foam;
2. Determine the origin of the foam constituents; and
3. Recommend further studies to reduce or eliminate the foaming condition.

A four-phase sampling and analysis program was undertaken to study the river foaming problem.

1. Phase I: The purpose of Phase I was to determine if resin and fatty acids were present in a pulp, paper, and paperboard mill's effluent. The International Paper Company's Androscoggin Mill in Jay, Maine was selected as the pulp and paper mill for sampling. Analysis was performed by gas chromatography/mass spectrometry (GC/MS) utilizing analytical procedures developed by the EPA.

   Between Phase I and II a comparison of gas chromatography (GC) and GC/MS analytical results was made. It was found that GC analyses provided accurate, reliable results for a much lower cost than GC/MS analysis could provide. This was important to the study because had GC/MS been required, the higher cost would have severely limited the number of analyses that could be performed. This conclusion was borne out by a GC versus GC/MS comparison in another EPA study (2).

2. Phase II: This phase began a process which was intended to ultimately lead to meeting study objective 2 by developing "treatment technologies capable of yielding non-foam mill effluents." Battelle and DEP results had not demonstrated the pulp, paper, and paperboard industry was solely responsible for the foaming condition on the Androscoggin River. However, it was known that pulp, paper, and paperboard mill effluents foamed, so the first step was to sample in a pulp, paper, and paperboard mill to find the sources of the surfactants. This would help by determining what to treat and where to treat it, the rationale being that it would be more economical to treat a single process stream than to treat all of the process streams together. Under Phase II, sampling and analysis was continued at International Paper Company's Androscoggin Mill by analyzing 24-hour composite samples from six locations.

3. Phase III: This phase continued the work of Phase II studying three sample locations at International Paper Corporation's Androscoggin Mill in more detail. The object was to observe the day to day variability in the mill processes and to check the affect of various parameters on foaming tendency of water samples collected in the mill. Parameters were varied that were known to effect foaming tendency, including pH, addition of water softener (hex-

ametaphosphate), addition of sodium, and addition of a surfactant (Joy dishwashing detergent). The pH has a dramatic effect on the foaming tendency of surfactants. Water softeners have a higher affinity for metallic ions than surfactants. If left in solution, metallic ions complex with certain surfactants rendering them insoluble. Therefore, the addition of water softeners allows any surfactants that are present to more readily create foam. Sodium increases the ionic strength of a solution. Therefore, sodium lowers the critical concentration of a surfactant required to create foam. When surfactants are present in solution below their critical concentration (for creating foam), foam will not form. However, foam may be created by adding more surfactant, such as Joy dishwashing detergent. The foam then concentrates surfactants from both the Joy and the solution's original surfactants.

During Phase II, the bleach plant effluent samples unexpectedly foamed. Two groups of surfactants were found to be responsible: methylene blue active substances (MBAS) and polyaromatic pulping products. Therefore, during Phase III, analyses was performed for these surfactants as well as for resin and fatty acids.

4. Phase IV: It was anticipated that this phase would entail performing a pilot scale foam generation system study. However, the parallel ongoing analysis by Battelle of the terminal river foam had not demonstrated that the pulp, paper, and paperboard industry was solely responsible for the river foam. Therefore, it was inappropriate to do a pilot plant study at International Paper Company's Androscoggin Mill. Instead, the Phase III program was continued on a larger scale by including the sampling and analysis of the major industrial and municipal point sources on the Androscoggin River in Maine.

Foaming is a complex phenomenon. Its composition may include anions, cations, resin acids, fatty acids, and numerous other elements. All of the compounds that form foam on the Androscoggin River have not been identified, nor is there an EPA-approved test to determine the foaming potential of wastewater. However, the redefined objectives of this study have been partially met, and we are much closer to an understanding of foam, and to developing an eventual solution to the problem.

The general accomplishments of this study are as follows. A literature review entitled "Foam and Its Elimination" was completed in April 1979, and is appended. In addition, Battelle Columbus Laboratories of Ohio analyzed collapsed river foam samples in order to chemically characterize the materials present. A large percentage of the materials can be accounted for by summation of individual analyses, as shown in Battelle's report, also appended. However, of these materials that are extractable, only a few percent are accounted for by summation of the individual compounds identified by gas chromatography/mass spectrometry (GC/MS). It is probable that a large portion of the extracted material decomposed in the GC injector even after derivatization.

The State of Maine Department of Environmental Protection (DEP) also performed a study of the sources and causes of foam along the entire length of the Androscoggin River. Generally, organic concentrations were found to be low or undetectable in ambient waters, but the data are insufficient to produce obvious or easily substantiated conclusions. The DEP report is also appended.

SECTION 2
CONCLUSIONS AND RECOMMENDATIONS

The data presented in this report clearly documents the complexity of the foaming problem on the Androscoggin River. An extremely complex chemical composition of riverine as well as upstream pristine foam, ambient factors, and contribution by various point sources all have yet to be fully explored.

At this point in the study of Androscoggin River foam, it has not been determined whether any of the industrial or municipal point sources acting alone, or in combination with one another and/or ambient conditions, is responsible for the foaming condition on the river.

CONCLUSIONS

Detailed conclusions may be found in Sections 3 and 4. The following is a summary of conclusions:

The Chemical Composition of Foam: River foam downstream of Topsham was found to contain a plethora of organic matter, including neutrals, weak acids, polyaromatic pulping products, as well as inorganics. "Pristine" foam (foam upstream of all points sources) lacked certain of the above components, such as resin acids and chloroguaiacols, but was also found to be extremely complex. An attempt to mass balance a downstream sample of foam accounts for approximately 50 percent of both organic and inorganic matter.

Origin of Foam Constituents: The Rumford-Mexico and Lewiston-Auburn municipal treatment plant effluents did not produce collectible quantities of foam when subjected to pneumatic treatment. Most of the pulp, paper, and paperboard mill treatment plant effluent samples produced foam when subjected to pneumatic treatment. The Lisbon municipal treatment plant effluent (which contained paperboard mill treated wastewater) also foamed. Samples foamed for up to one-half hour and then stopped. Collectible foam was found to be enriched in methylene blue active substances (MBAS), while polyaromatic pulping products were not concentrated in the foam.

Factors Affecting Foam Formation: International Paper's Androscoggin Mill was sampled at the brownstock washer effluent (BS) and the bleach plant acid sewer (BP), as well as at the secondary clarifier effluent (FE). The BS effluent contained resin and fatty acids, methylene blue active substances (MBAS), and polyaromatic pulping products, while the BP effluent contained only MBAS and polyaromatic pulping products. Factors known to affect foam formation, including pH, sodium, hexametaphosphate, and addition of surfactants were analyzed for their effect on BS, BP, and FE samples. A summary table follows:

DATA SUMMARY OF FACTORS AFFECTING FOAM FORMATION
AT INTERNATIONAL PAPER CORPORATION, JAY, MAINE

Sample Location	Treatment that enhanced foaming tendency*	Increased removals by foaming of: MBAS†	Resin and fatty acids	Polyaromatic pulping products
BS	1,2,3,4	1,2,3	1,2,3,4	No
BP	4	3	Limited data	No
FE	1,2,4‡	§	§	4

*Treatment affects of the following four conditions were examined:

1 = adjusting pH
2 = addition of sodium sulfate
3 = addition of sodium hexometaphosphate
4 = addition of a surfactant (Joy dishwashing detergent)

†Because the surfactant addition, treatment 4, resulted in high levels of MBAS addition, removals of relatively low levels of MBAS in the original solution could not be assessed.

‡The FE did not foam without treatment.

§Original levels were too low to determine affects of treatment.

From the summary table it may be concluded that several parameters increase the foaming tendency of the BS and FE effluents. Only the addition of surfactant increased the foaming tendency of BP. This was expected. The adjustment of pH or the addition of chelating agents should not enhance the BP effluent foaming tendency because strongly acidic or neutral surfactants are not affected by these parameters. The same parameters that enhanced foaming tendency in the BS effluent, also increased removals of MBAS and resin and fatty acids by foaming. In the FE the data shows removals of polyaromatic pulping products by addition of a surfactant.

RECOMMENDATIONS

In order to solve the Androscoggin River foaming problem, the sources and chemistry of the foam must be identified. Also, a better method of testing samples for foaming tendency would help in determining the relative contributions.

A better foaming tendency test, alone, however, may not solve the problem economically. Mechanical defoaming equipment has been developed that is effective, but economically prohibitive. Therefore, another reason for studying foam chemistry is to determine if there are major foam constituents that could be selectively removed at a reduced cost.

The following seven points suggest further areas of study of the foaming problem on the Androscoggin River:

1. Elucidation of the chemical composition of foam. The Battelle and DEP results indicate that a considerable amount of material in Androscoggin river foam remains to be characterized. Low recoveries of organics, both neutral and acidic, in the extractable fraction suggests that HPLC/MS should be employed. The aqueous phase, with its apparently substantial level of unidentified MBAS should also be studied further using more sophisticated techniques such as HPLC/MS. Additional inquiry into the variability of chemical composition of foam at various points on the river should lead to a clearer understanding of the factors contributing to the foaming condition.
2. The results from chemical analysis of various point sources, ambient foams, and pristine foams should be correlated to determine the origin of contributing surfactants.
3. Determination of the chemical composition of MBAS in various point sources: All samples analyzed contained MBAS which can be strong surfactants. It should also be determined whether the MBAS are of domestic or industrial origin. The action of sulfide ion to accelerate dissolution of wood to release cellulose fibers has been known for many years (3-4). The acceleration is chemically described as a reaction between the sulfide ion and lignins. Subsequent to the direct reaction of sulfide in the digester, oxidative reactions can lead to the production of polyaromatic pulping products. The commercial preparation of lignosulfates gave a weak MBAS reaction. It is possible that different forms of organic sulfates and sulfonate surfactants could be produced in the pulping process that would be positive to the MBAS test.
4. Testing of the foamability of pure solutions containing various levels and combinations of the compounds present in river foam should be performed.
5. Development of improved methods for analysis of surfactants: The present methods for the levels of surfactants of the type found in river foam require improvement. In particular, the MBAS, polyaromatic pulping products, and neutral surfactants will require high resolution HPLC coupled with MS for resolution and identification.

6. The affect of ambient conditions, i.e. flows, temperature, humidity, and wind, on the persistence of river foam: DEP has shown a possible correlation to river flow and foaming, but substantiating data has not been collected.
7. Further work should be performed on the following: foam composition as it relates to the possible concentration of toxic substances from the river and its sediments; the resolution, transport and deposition of priority pollutants and other substances by surfactant aggregates; stabilization or destabilization of toxic pollutants and other substances by surfactant aggregates; and the synergistic effect of toxicity of various priority pollutants and other substances when in the presence of surfactants (5,6,7,8).
8. A method for assessing foaming tendency in ambient conditions should be developed. Two techniques were used in this study: a blender technique as outlined in ASTM D3519-76 and a pneumatic technique developed by B.C. Research. Both techniques are standard techniques that have been used by others. However, both failed to produce foam on some samples which would have been expected to foam because of the observed foaming condition in the river during sampling. Also, both techniques fail to detect trace amounts of surfactants. Therefore, a more sensitive technique should be developed.

SECTION 3
CHEMICAL COMPOSITION OF FOAM

During the period November 2, 1978 to June 28, 1979 an extensive sampling program was conducted by the State of Maine Department of Environmental Protection (DEP). Water samples were collected from Errol, New Hampshire to Topsham, Maine from both point and ambient sources on the river as shown on Figure 1. Foam samples were analyzed for various organic and inorganic components, and their composition was variable. Foam from pulp, paper, and paperboard mill effluents and sources downstream of paper mill discharges contained resin and fatty acids, and chloroguaiacols. The "pristine" foams from Errol Dam and the Little Androscoggin River did not contain detectable resin acids and chloroguaiacols. Foams described as pristine are those found upstream of any point sources.

Resin and fatty acids identified included linoleic, linolenic, oleic, 9,10-dichlorostearic, stearic, palmitic, myristic, pimaric, abietic, dehydroabietic and isopimaric. The levels in collapsed foam ranged from 100 to 300 ug/l for the chloroguaiacols to several mg/l for the individual resin and fatty acids. Summation of the GC/MS identifiable organics accounted for 1 to 20 percent of the total carbon content. All foams contained phosphorus, sodium, potassium, calcium, and magnesium, with the "pristine" foams having a higher ratio of organic to inorganic matter than the foams collected below and from municipal/ industrial treatment plant discharges. An attempt to mass balance a sample of foam collected at Topsham, Maine left approximately 50 percent of both organic and inorganic matter unaccounted for. A copy of the final DEP report is included as Appendix D.

On May 5, 1979 a foam sample was collected at Topsham, Maine. The sample was collapsed to liquid which represented 3 to 4 percent of the original foam volume. The liquid was analyzed for total organic carbon (TOC), acidified and extracted to yield an aqueous and organic phase. Both phases were analyzed by Battelle Laboratories with the following summarized results:

Approximately 80 percent of the organic material was extractable under acidic conditions. A large portion of the material which resisted extraction was methylene blue active. The resistant material showed low levels of carbohydrate, nitrogen, and phenolic reactivity.

The extractable material was exhaustively analyzed by pH fractionation/ derivatization followed by capillary column GC/MS. The pH fractionation revealed that over 90 percent was neutral, and less than 10 percent car-

FIGURE 1
SAMPLE LOCATIONS

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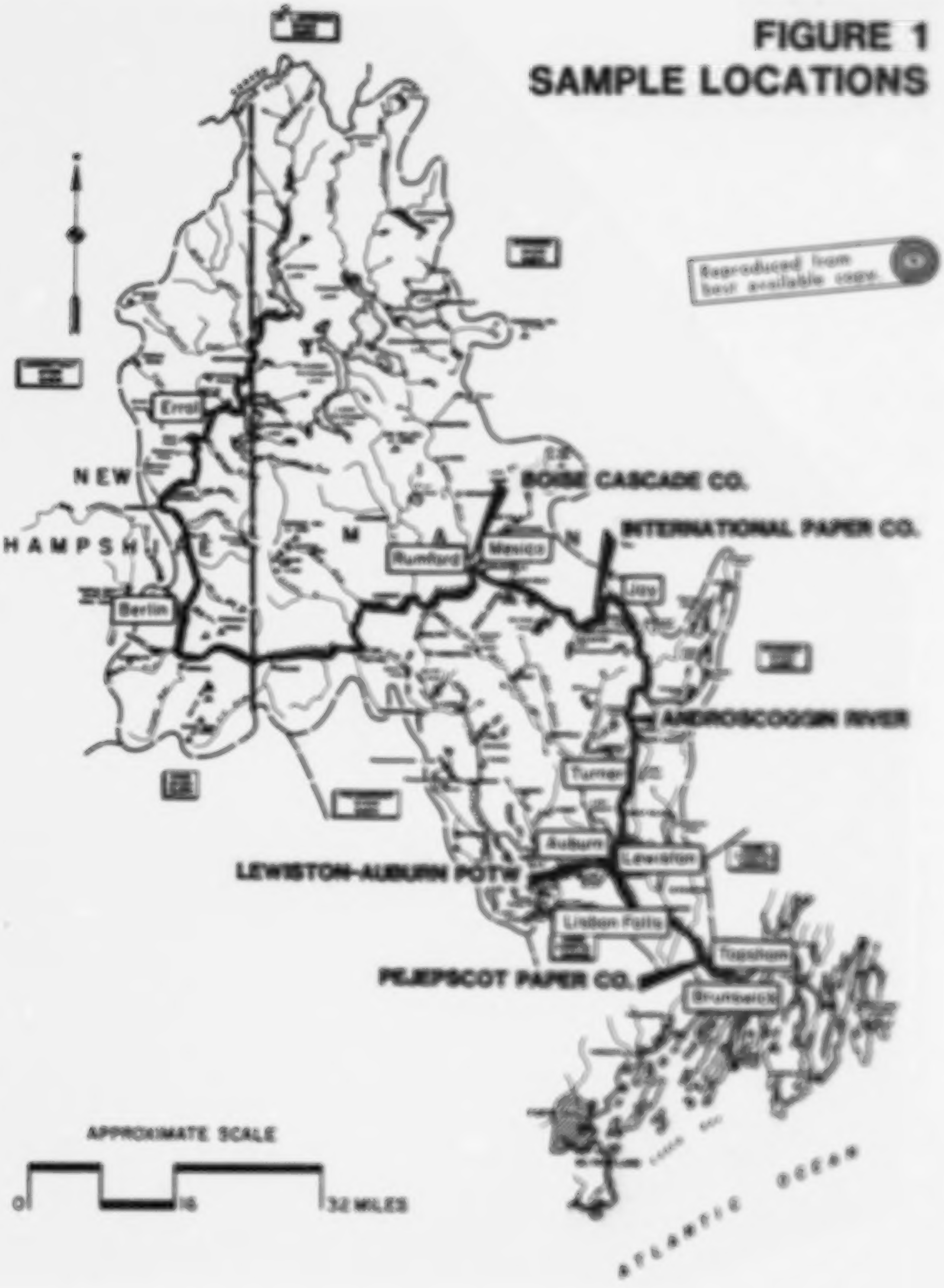
Errol
NEW HAMPSHIRE
M
Berlin
Rumford
Mexico
BOISE CASCADE CO.
INTERNATIONAL PAPER CO.
Jay
ANDROSCOGGIN RIVER
Turner
Auburn
Lewiston
LEWISTON-AUBURN POTW
Lisbon Falls
Topsham
PEJEPSCOT PAPER CO.
Brunswick
APPROXIMATE SCALE
0
16
32 MILES
ATLANTIC OCEAN

boxylic acids. Gas chromatography of the neutral fraction showed over 100 separate components. Mass spectra of the 36 largest peaks revealed an aldehyde analogue of dehydroabietic acid as the largest component, and an aldehyde analogue of abietic acid as the second largest component. The third and fourth largest components could not be identified. Of the 36 largest peaks, 9 appeared as resin acid based neutrals with partially reduced phenanthrene or naphthalene nucleii, 6 appeared to be fatty alcohols, both saturated and unsaturated, 4 were likely phenolic or phenoxy lignin breakdown products, 2 were unsaturated hydrocarbons and 9 were unidentified. Eighty to ninety percent of the GC analyzable neutral components were present as a plethora of species at relatively low concentrations (1 to 5 percent of the most concentrated component). The acid fraction principally contained resin acid-related carboxylic acids. Major constituents were abietic, dehydroabietic, pimaric or isopimaric, chlorinated abietics, and chlorinated guaiacols. C-6 to C-26 fatty acids were detected. There were many compounds whose structures could not be specified but were clearly resin acid-related compounds. Additional gas chromatography and mass spectral searches were not performed due to time and budget limitations.

Using an averaged response factor for resin and fatty acids it was estimated that 2 to 8 percent of the neutral and 5 to 11 percent of the acidic material injected were recovered in gas chromatography. Copies of the reports of analytical results of work done by Battelle Laboratories are included as Appendix C.

In summary, the analytical work has revealed the extremely complex chemical makeup of Androscoggin River foam. Foam from downstream reaches of the river contain a plethora of organic matter including neutrals, weak acids, polyaromatic pulping products, as well as inorganics. "Pristine" foam lacked certain components, such as resin acids, but is also extremely complex. A significant portion of the organic and inorganic material remains unidentified. Further inquiry will be required to fully identify the chemical composition of Androscoggin River foam.

SECTION 4
ORIGIN OF FOAM CONSTITUENTS

A four-phase sampling and analysis program was undertaken to study the river and the foaming problem. The first three phases consisted of collecting data at International Paper Company's Androscoggin Mill in Jay, Maine. Phase IV expanded the data base by performing a sampling and analysis program at all the major industrial and municipal point sources on the Androscoggin River in Maine.

PHASE I - SCOPE

On April 20, 1979, Phase I began with six one-hour composite samples being collected from the decker filtrate and treatment plant effluent at International Paper Company's Androscoggin Mill in Jay, Maine. The decker filtrate sample served as an analytical check because it was known that resin and fatty acids are present in softwood washing operations. The samples were sent to Gulf South Research Institute (GSRI) in New Orleans, Louisiana for analysis to determine if certain weakly acidic surfactants were present in the effluent sample. The weakly acidic surfactant compounds were chosen from a review of the literature (the Jordan Company's literature review, appended), and from compounds detected during the Jordan Company's industrial screening analysis for the EPA's Best Available Technology (BAT) review program in the pulp, paper, and paperboard industry.

DISCUSSION OF PHASE I RESULTS

GSRI's Phase I GC/MS results from the samples collected April 20, 1979 are as follows:

TABLE 1. PHASE I RESULTS

Compound	Decker filtrate (μg/l)	Final effluent (μg/l)
oleic acid	2,200	1,300
linoleic acid	1,900	71
linolenic acid	250*	230*
pimaric acid	±	‡
isopimaric acid	240	120
dehydroabietic acid	220	50
abietic acid	1,900	400
fatty acids	2,700	ND
percent recovery of stearic acid	66	34

* = Characteristic ion present at predicted retention time, but confirmatory ions missing.

‡ = GC/MS data carefully re-examined and this compound definitely not present.

ND = Not detected.

The "other" fatty acid concentration reported was quantified from m/e 117, an ion common to all fatty acids. The average response ratio was calculated from a composite fatty acid standard. No "other" resin acids were detected. It should also be noted that the secondary clarifier effluent was not representative of normal operations. The entire plant's flow was being processed through one instead of two secondary clarifiers. Therefore, the secondary clarifier effluent would not be expected to be as high a quality as with normal operation.

As shown on Table 1, GSRI detected all of the postulated weakly acidic surfactants except pimaric acid. These preliminary GSRI results and results from the DEP ambient sampling revealed the presence of resin and fatty acids (which are weakly acidic surfactants) in river foam samples. Upstream of all the point discharges resin acids were not detected.

As a result of the Phase I sampling and analysis program, it was demonstrated that:

1. wastewater at the International Paper Company's Androscoggin Mill contains surfactants capable of causing foam; and
2. the Androscoggin River foam below International Paper Company's Androscoggin Mill contains some of the same surfactant compounds found in International Paper Company's wastewaters.

Phase I was a screening program that showed that the International Paper Company's Androscoggin Mill effluent contained some of the same surfactants present in the river foam. Therefore, it was concluded that a more detailed study was both feasible and warranted. Phase II began the more detailed study.

PHASE II - SCOPE

The Phase II sampling program was conducted during the week of June 29, 1979 at International Paper Company's Androscoggin Mill. Twenty-four hour composite samples were collected at each of the following six locations in the softwood pulping operation, as shown on Figure 2. Softwood pulping is known to liberate more resin and fatty acids than hardwood pulping.

1. process water supply (Androscoggin River);
2. decker filtrate;
3. softwood brownstock washer effluent;
4. bleach plant acid effluent;
5. splitter box upstream of two primary clarifiers; and
6. secondary treatment system effluent (upstream of foam dissipator).

Samples were caused to foam by a blender technique, where possible, in accordance with procedures outlined in ASTM D3519-76. Both the wastewater and the defoamed wastewater were analyzed to identify the weakly acidic surfactants known to be produced by the pulping process. In this way, a crude materials accounting of compounds with potential to create foam could be established. Having established this, the intent of Phase II was to zero in on those process and waste streams containing the majority of foamants for an in-depth investigation during Phase III.

DISCUSSION OF PHASE II RESULTS

As shown in Table 2, process water supply samples did not produce foam by the technique employed. The decker filtrate and brownstock washer effluents contained several mg/l of various resin and fatty acids. Also, the sample pH's were alkaline and foamed in varying degrees from 3 to 16.2 percent of the original solution volume. Modest reductions in levels of resin and fatty acids were observed in the water samples following foam separation. Day to day levels of the compounds studied were relatively constant. Bleach plant effluent contained less than one mg/l of various resin and fatty acids, was strongly acidic and foamed from 6.5 to 16.6 percent of the original solution volume. A reduction in fatty acid concentration occurred during foam generation. Primary clarifier influent (raw mill wastewater) contained values in the order of mg/l levels of resin and fatty acids, was alkaline pH, and foamed from 11.3 to 33.3 percent of the original solution volume. Modest reductions in resin and fatty acids were observed during foam generation.

The reductions in levels of weakly acidic surfactants during foam generation in the brownstock washer effluents and the primary clarifier

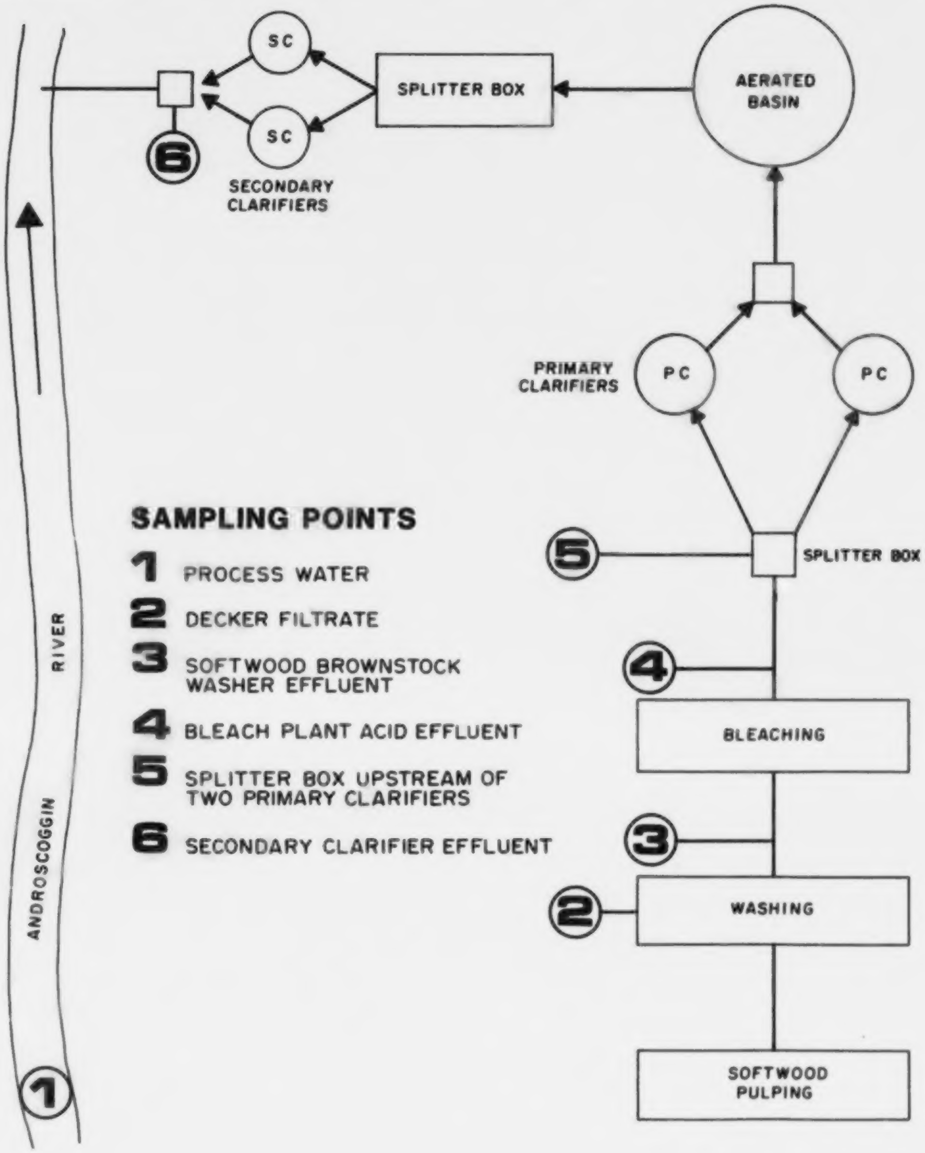
SC
SC
SPLITTER BOX
AERATED BASIN
6
SECONDARY CLARIFIERS
PRIMARY CLARIFIERS
PC
PC
SAMPLING POINTS
1 PROCESS WATER
2 DECKER FILTRATE
3 SOFTWOOD BROWNSTOCK WASHER EFFLUENT
4 BLEACH PLANT ACID EFFLUENT
5 SPLITTER BOX UPSTREAM OF TWO PRIMARY CLARIFIERS
6 SECONDARY CLARIFIER EFFLUENT
5
SPLITTER BOX
4
BLEACHING
3
2
WASHING
SOFTWOOD PULPING
ANDROSCOGGIN RIVER
1

FIGURE 2
SCHEMATIC OF SAMPLING POINTS AT INTERNATIONAL PAPER CORPORATION'S ANDROSCOGGIN MILL IN JAY, MAINE

TABLE 2. PHASE II DATA

EPA NO.	COMPOUND	SAMPLE NUMBER 12	12F	13	13F	14	14F	15	15F	22	23	24	25
134	oleic acid	5,530	2,870	3,575	2,320	3,920	2,090	5,560	2,120	ND	80	105	ND
135	linoleic acid	8,134	4,500	7,120	3,715	8,430	4,900	10,540	4,610	ND	310	205	ND
136	linolenic acid	ND	ND	60	ND	ND	ND	1,520	540	ND	153	59	ND
133	pimaric acid	ND	65	470	200	ND	ND	2,220	820	ND	ND	ND	ND
--	sandaracopimaric acid	640	770	415	460	230	390	960	1,240	ND	ND	ND	ND
132	isopimaric acid	12,400	520	12,730	9,460	9,990	11,340	17,600	10,630	ND	ND	116	ND
130	abietic acid	8,800	75	8,040	7,340	9,360	80	13,960	8,630	ND	ND	154	ND
131	dehydroabietic acid	4,700	190	4,660	3,400	5,910	4,090	9,020	4,450	ND	ND	59	ND
139	monochlorodehydroabietic acid	ND	320	ND	ND	ND	370	36,450	18,640	ND	ND	ND	ND
140	dichlorodehydroabietic acid	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	Foam (%)		8	ND	4.9		4.9		4.9				
	pH		10.3		11.2		10.0		10.1				
	Recovery Heptadecanoic Acid (%)	73	105	68	65	62	75	72	64	59	46	49	60
	Location	decker effluent	decker effluent	decker effluent	decker effluent	decker effluent	decker effluent	decker effluent	decker effluent	process water	process water	process water	process water
	Date Sampled	6-25	6-25	6-26	6-26	6-27	6-27	6-29	6-29	6-25	6-26	6-27	6-28

Analytical data - resin and fatty acids: All values in ug/l corrected for internal standard recovery.
ND = Not detected
12F, 13F, etc = foamed samples.

TABLE 2. Phase II Data, Cont.

EPA NO.	COMPOUND	SAMPLE NUMBER											
		32	32F	33	33F	34	34F	35	35F	42	42F	44	44F
134	oleic acid	9,230	7,060	37,900	13,330	10,120	4,760	11,430	2,620	270	74	150	39
135	linoleic acid	10,300	7,515	47,280	20,810	16,960	9,320	13,800	3,300	720	430	930	78
136	linolenic acid	140	ND	530	ND	2,780	140	ND	ND	150	ND	430	ND
133	pimaric acid	ND	ND	7,670	ND	7,920	4,110	ND	ND	ND	ND	ND	ND
--	sandaracopimaric acid	1,000	700	3,720	ND	6,740	540	230	ND	ND	ND	ND	ND
132	isopimaric acid	11,225	11,000	26,750	25,610	25,140	7,590	23,160	6,120	ND	ND	ND	ND
130	abietic acid	12,050	12,100	31,925	28,010	19,320	7,090	22,380	5,450	ND	ND	ND	ND
131	dehydroabietic acid	7,100	4,040	19,150	11,330	10,770	4,640	9,440	2,410	ND	ND	ND	ND
139	monochlorodehydroabietic acid	ND	ND	ND	ND	5,110	ND	ND	ND	ND	ND	ND	ND
140	dichlorodehydroabietic acid	ND	ND	ND	ND	1,000	ND	ND	220	ND	ND	ND	ND
	Foam (%)		3		16.2		4.9		6.5		6.5		12.9
	pH		13.0		11.6		11.0		10.7		1.0		1.3
	Recovery Heptadecanoic Acid (%)	80	67	91	21	72	22	91	70	56	44	96	36
	Location	brownstock effluent	brownstock effluent	brownstock effluent	brownstock effluent	brownstock effluent	brownstock effluent	brownstock effluent	brown stock effluent	bleach plant effluent	bleach plant effluent	bleach plant effluent	bleach plant effluent
	Date Sampled	6-25	6-25	6-26	6-26	6-27	6-27	6-28	6-28	6-25	6-25	6-27	6-27

Analytical data - resin and fatty acids: All values in ug/l corrected for internal standard recovery.

ND = Not detected

32F, 33F, etc = foamed samples.

TABLE 2. Phase II Data, Cont.

EPA NO.	COMPOUND	SAMPLE NUMBER 45	45F	52	52F	53	53F	54	54F	55	55F	62-65	
134	oleic acid	ND	ND	2,590	1,575	1,245	1,430	7,410	1,790	2,630	1,100	ND	
135	linoleic acid	ND	ND	3,080	1,440	1,262	1,130	7,510	1,460	5,700	1,170	ND	
136	linolenic acid	ND	ND	ND	ND	ND	ND	ND	ND	2,740	ND	ND	
133	pimaric acid	ND	ND	60	ND	ND	ND	ND	ND	6,940	ND	ND	
--	sandaracopimaric acid	ND	ND	ND	ND	ND	120	ND	110	1,580	ND	ND	
132	isopimaric acid	ND	ND	ND	2,300	1,370	2,150	8,150	2,240	ND	ND	ND	
130	abietic acid	ND	ND	ND	2,440	1,960	1,850	11,660	140	3,620	2,620	ND	
131	dehydroabietic acid	ND	ND	2,475	1,970	1,585	1,610	9,430	2,275	3,470	4,410	ND	
139	monochlorodehydroabietic acid	ND	ND	ND	1,675	ND	ND	ND	ND	48,590	11,350	ND	
140	dichlorodehydroabietic acid	ND	ND	90	ND	ND	ND	ND	110	ND	ND	ND	
	Foam (%)		16.6		11.3		11.6		33.3		23.7		
	pH		0.5		11.0		9.6		8.2		9.2		
	Recovery Heptadecanoic Acid (%)	72	68	56	67	42	41	49	70	93	75	67-95	
	Location	bleach plant	bleach plant	primary clarifier influent	primary clarifier influent	primary clarifier influent	primary clarifier influent	primary clarifier influent	primary clarifier influent	primary clarifier influent	primary clarifier influent	secondary clarifier effluent	
	Date samples	6-28	6-28	6-25	6-25	6-26	6-26	6-27	6-27	6-28	6-28	6-25	6-28

Analytical data - resin and fatty acids: All values in ug/l corrected for internal standard recovery.

ND = Not detected
45F, 52F, etc = foam samples.

influent suggested that these materials may be contributing to the foam produced in the river. The reductions observed also indicated that mechanical foam generation may be a viable pretreatment for removal of weakly acidic surfactants from kraft pulping wastewaters. The bleach plant effluent foamed at low pH suggesting surfactants other than the weakly acidic group, such as neutrals and/or strongly acidic ones (polyaromatic pulping products). The primary clarifer influent demonstrated the highest foaming tendency although this stream contained somewhat lower levels of resin and fatty acids then the brownstock washer effluents. The combination of various mill waste streams, i.e., brownstock washer and bleach plant effluent, and their surfactants, could result in a synergistic effect producing more foam than in an individual waste stream.

None of the compounds tested for were detected in the secondary clarifier effluent, nor did the samples foam when subjected to the blender technique. Treatment plant final effluent contained less than 5 ug/l of the various resin and fatty acids. It is important to note that during this sampling large doses of alum were being used, which could reduce the levels of surfactant and reduce foaming tendency by increasing effluent "hardness" (i.e., the higher the hardness the greater the amount surfactant necessary to cause foam).

As a result of the Phase II study, it was discovered that bleach plant effluent also foamed even though there were very small concentrations of fatty acids and no resin acids. Since weakly acidic surfactants will not foam in a strongly acidic environment, such as with the three bleach plant effluent samples collected, and since basic surfactants would have no reason for being present in the bleach plant effluent, it was concluded that analysis must be performed for strongly acidic surfactants. The following section on Phase III details this analysis.

PHASE III - SCOPE

The Phase III sampling program was conducted during the week of October 23, 1979 at International Paper Company's Androscoggin Mill. Samples were collected from the bleach plant acid sewer, the brownstock washer effluent, and the effluent from the secondary clarifier. The brownstock washer effluent was resampled because it was found to have the highest concentration of resin and fatty acids of all locations sampled in Phase II. The secondary clarifier effluent was resampled because it represents the discharge to the river. This more detailed sampling and analysis at the Androscoggin Mill helped to expand the data base developed in Phase II. Also, affects of such conditions as pH, ionic strength, chelating agents (water softeners), and additional surfactants were examined by foaming the samples by the ASTM D 3519-76 blender technique used in Phase II. A surfactant chemist, Daniel Armstrong, Ph.D., was subcontracted to perform the analysis for strongly acidic surfactants in the bleach plant effluent.

DISCUSSION OF PHASE III DATA

The data summarized in Table 3 shows that brownstock washer effluent contained several mg/l of various resin and fatty acids, methylene blue active substances (MBAS), and polyaromatic pulping products. Samples were alkaline, and foamed from 3 to 8 percent (average 5.2) of the original solution volume. This result varies from Phase II because of process variations within International Paper Company's Androscoggin Mill. Reduction of pH and/or addition of sodium to 0.18 molar (M) enhanced foaming tendency. Addition of hexametaphosphate to 100 mg/l enhanced foaming tendency, only at alkaline pH. Upon foam generation and removal, modest reductions in levels of MBAS occurred only at alkaline pH. Sodium increased removal of MBAS at alkaline and neutral pH, but had no affect at a pH of 3. Hexametaphosphate increased removal of MBAS at all pH's. Little affect on levels of polyaromatic pulping products was observed under any conditions tested. Modest enhancement of reductions in resin and fatty acids were observed by the addition of sodium, hexametaphosphate and Joy, as well as neutralization. The removal of resin and fatty acids did not improve when sodium or Joy in combination with wastewater neutralization was tested.

As shown in Table 4, the bleach plant effluent contained low (generally less than 100 ug/l) levels of resin and fatty acids, several mg/l of MBAS and several hundred mg/l of polyaromatic pulping products. The MBAS concentrations were highly variable, while the polyaromatic pulping products were almost always greater than 200 mg/l (as polyfon-H standard, Appendix A). It was strongly acidic, and foamed from 5 to 10 percent (average 8.2) of the original solution volume. Earlier sampling and analysis under Phase II yielded foaming of 6.5 to 16.5 percent (average 12.0) of the original solution volume. Variations in International Paper Company's process may explain the reason for the variation in test results. pH adjustment and/or in conjunction with the addition of sodium to 0.18M or hexametaphosphate to 100 mg/l had little or no effect on foaming tendency. Due to the limited number of data points and low levels of resin and fatty acids, no conclusions can be drawn regarding the effect of foam generation on reducing resin and fatty acid concentrations. No effect on polyaromatic pulping products was observed, however, an apparent enhancement of removal of MBAS occurred on neutralization in the presence of hexametaphosphate.

As shown in Table 5, the final treatment plant effluent contained low (less than 100 ug/l) levels of resin and fatty acids, mg/l levels of MBAS, and over 100 mg/l of polyaromatic pulping products. It was neutral pH, and did not foam by the blender technique employed. Alkalinization did not enhance foaming tendency, but acidification did. Addition of sodium dramatically enhanced foaming tendency regardless of pH.

TABLE 3. PHASE III DATA SUMMARY - BROWNSTOCK WASHER EFFLUENT

Treatment	Foam (%)	PERCENT REDUCTION BY FOAM REMOVAL												
		OL	LMOL	LMOLN	PIM	SPIM	IPIM	AB	DAB	Cl-DAB	Cl_2-DAB	SDS*	DBS*	Polyfon H*
None	5.2^5	41.5^1	29.3^1	$>90^1$	$>90^1$	$>90^1$	0^1	23.3^1	28.3^1	$>90^1$	ND	35^1	44^1	31^1
Na+	12.5^4	70.5^1	81^1	-	-	$>90^1$	57^1	54^1	52^1	ND	ND	-	-	-
Polyphos	16.8^5	46^1	0^1	$>90^1$	$>90^1$	ND	0^1	49^1	64^1	$>90^1$	ND	$>90^1$	$>90^1$	0^1
Joy	24.4^5	93^2	$>90^2$	$>90^1$	-	ND^1	54^1	$>90^1$	64^1	ND^1	ND^1	-	-	-
pH 7	11.8^5	81.5^2	83^2	$>90^1$	$>90^1$	$>90^1$	54^1	76.5^2	61.5^2	$>90^1$	ND^1	0^1	0^1	0^1
Na+	22.4^5	34^2	41^2	ND^1	ND^1	ND^1	55^1	45^1	57^1	ND^1	ND^1	$>90^2$	$>90^2$	0^1
Polyphos	14.2^5	14.2^5	14.2^5	14.2^5	14.2^5	14.2^5	14.2^5	14.2^5	14.2^5	14.2^5	14.2^5	14.2^5	14.2^5	14.2^5
Joy	17.6^5	64^3	60^3	ND^3	ND^2	$>90^1$	50^2	44^2	53^2	ND^2	ND^2	-	-	-
pH 3	8.6^5	8.6^5	8.6^5	8.6^5	8.6^5	8.6^5	8.6^5	8.6^5	8.6^5	8.6^5	8.6^5	8.6^5	8.6^5	8.6^5
Na+	12.2^5	83^1	$>90^1$	ND^1	ND^1	ND^1	55^1	61^1	53^1	ND^1	ND^1	0^1	0^1	-
Polyphos	7.8^5	7.8^5	7.8^5	7.8^5	7.8^5	7.8^5	7.8^5	7.8^5	7.8^5	7.8^5	7.8^5	$>90^1$	$>90^1$	20^1
Joy	13.5^4	13.5^4	13.5^4	13.5^4	13.5^4	13.5^4	13.5^4	13.5^4	13.5^4	13.5^4	13.5^4	13.5^4	13.5^4	13.5^4

Superscript indicates number of data points
ND = Not Detected
- = No data

TABLE 4. PHASE III DATA SUMMARY - BLEACH PLANT EFFLUENT

Treatment	Foam (%)	PERCENT REDUCTION BY FOAM REMOVAL												
		OL	LNOL	LNOLN	PIM	SPIM	IPIM	AB	DAB	Cl-DAB	Cl_2-DAB	SDS	DBS	Polyfon H
None	8.2^5	75.5^2	$>90^2$	ND^4	$>90^2$	0^3	$>90^3$	64^2	$>90^3$	ND^4	ND^4	0^1	0^1	0^1
Na+	9.0^5	9.0^5	9.0^5	9.0^5	9.0^5	9.0^5	9.0^5	9.0^5	9.0^5	9.0^5	9.0^5	9.0^5	9.0^5	9.0^5
Polyphos	9.6^5	9.6^5	9.6^5	9.6^5	9.6^5	9.6^5	9.6^5	9.6^5	9.6^5	9.6^5	9.6^5	9.6^5	9.6^5	9.6^5
Joy	15^5	-	-	-	$>90^2$	$>90^2$	$>90^3$	$>90^2$	$>90^2$	ND^4	ND^4	-	-	-
pH 7	6.8^5	6.8^5	6.8^5	6.8^5	6.8^5	6.8^5	6.8^5	6.8^5	6.8^5	6.8^5	6.8^5	6.8^5	6.8^5	6.8^5
Na+	11.4^5	ND^1	ND^1	ND^1	ND^1	ND^1	$>90^1$	$>90^1$	ND^1	$>90^1$	$>90^1$	-	-	-
Polyphos	7.4^5	ND^1	ND^1	ND^1	0^1	$>90^1$	53^1	$>90^1$	0^1	ND^1	ND^1	$>90^1$	$>90^1$	26^1
Joy	15.2^5	52^1	0^1	ND^2	$>90^1$	$>90^1$	$>90^2$	66^1	$>90^1$	$>90^1$	$>90^1$	-	-	-
pH 10	10^5	ND^1	ND^1	ND^1	$>90^1$	0^1	$>90^1$	$>90^1$	$>90^1$	ND^1	ND^1	-	-	-
Na+	9.2^5	9.2^5	9.2^5	9.2^5	9.2^5	9.2^5	9.2^5	9.2^5	9.2^5	9.2^5	9.2^5	9.2^5	9.2^5	9.2^5
Polyphos	6.6^5	6.6^5	6.6^5	6.6^5	6.6^5	6.6^5	6.6^5	6.6^5	6.6^5	6.6^5	6.6^5	6.6^5	6.6^5	6.6^5
Joy	22.2^5	ND^1	ND^1	ND^1	ND^1	ND^1	$>90^1$	$>90^1$	ND^1	$>90^1$	$>90^1$	-	-	-

Superscript indicates number of data points
ND = Not Detected
- = No data

TABLE 4 - PHASE III DATA SUMMARY - BLEACH PLANT/BROWNSTOCK EFFLUENTS - continued

		PERCENT REDUCTION BY FOAM REMOVAL												
Mix Ratio BP/BS	Foam (%)	OL	LNOL	LNOLN	PIM	SPIM	IPIM	AB	DAB	Cl-DAB	Cl_2-DAB	SDS	DBS	Polyfon H
1:1	16.3^6	60^2	84^2	$>90^1$	>90	0^1	29^2	33^2	43^2	ND^2	ND^2	0^1	0^1	0^1
2:1	10^6	$>90^2$	$>90^2$	$>90^1$	$>90^1$	ND^2	48.5^2	53^2	60^2	ND^2	ND^2	0^1	0^1	0^1

Superscript indicates number of data points
ND = Not Detected
*Laboratory analysis performed by Daniel W. Armstrong, PhD.

1. Abbreviations: polyphos = 2 ml of 1% aqueous sodium hexametaphosphate to 200 ml sample
OL = Oleic acid
LNOL = Linoleic acid
LNOLN = Linolenic acid
PIM = Pimaric acid
SPIM = Sandaracopimaric acid
IPIM = Isopimaric acid
AB = Abietic acid
DAB = Dehydroabietic acid
DCS = Dichlorostearic acid

Percent foam determined by ASTM Method No. D3519-76.
Sample analyses of resin and fatty acids is as described in Appendix A, Materials and Methods.

ND = Not detected
Cl_2-DAB = Dichlorodehydroabietic acid
Cl-DAB = Monochlorodehydroabietic acid
SDS = Sodium dodecyl sulfate
DBS = Dodecylbenzene sulfonate
Polyfon H = Commercial sodium lignosulfonate
Joy = 1 ml of 5% aqueous solution of Joy dishwashing detergent to 200 ml sample
BP = Bleach plant acid sewer
BS = Brownstock washer effluent
FE = Secondary clarifier final effluent
Na_2SO_4 = 20 ml of 2M Na_2SO_4 to 200 ml sample

TABLE 5. PHASE III DATA SUMMARY - SECONDARY CLARIFIER EFFLUENT

Treatment	Foam (%)
None	0^5
Na*	14.2^5
Polyphos	0^5
pH 10	0^5
Na*	16^3
Polyphos	0^4
pH 3	6^4
Na*	18.6^5
Polyphos	6^4

Superscript indicates number of data points

Mixing bleach plant effluent with brownstock washer effluent at a ratio of 1:1 (volume to volume), and adjusting pH to 10, significantly enhanced foaming tendency over the original solutions. No effect was observed however, at a ratio of 2:1. In both cases, modest reductions in resin and fatty acids, and no affect on MBAS and polyaromatic pulping products was observed. This does not necessarily indicate that polyaromatic pulping products are not involved in foam production. It is possible that certain species of polyaromatic pulping products, which are more surface active than others, are concentrating in the foam. The analytical techniques used did not differentiate between species.

In the river study program and the Phase III sampling, it was noted that resin and fatty acids account for approximately 5 to 20 percent of the total carbon in the analyzed foam samples. Additional studies conducted by Daniel Armstrong, Ph.D., have found that polyaromatic pulping products and MBAS can account for a larger fraction of the organic material in the Androscoggin River foam than the fatty and resin acids.

A complete tabulation of Phase III data appears in Table 6.

PHASE IV - SCOPE

Initially, it was anticipated that a Phase IV pilot scale study would be conducted, utilizing a pilot foam generation system. This system was to be operated on two different wastewater streams at the International Paper facility. However, Battelle's analysis of the terminal river foam had not demonstrated that the pulp, paper, and paperboard industry was solely responsible for river foam. Therefore, it was concluded that the best approach to continuing the study would be to perform additional studies of major industrial and municipal point sources on the Androscoggin River.

The Phase IV sampling program was conducted during May, 1980. Samples were collected from the following Maine locations: Boise-Cascade, Rumford; International Paper Company, Jay; Lewiston-Auburn POTW; Lisbon POTW; and Pejepscot Paper Company, Topsham. These discharges represent the major municipal and industrial point sources along the Androscoggin River in Maine. There is an additional pulp, paper, and paperboard facility in Berlin, New Hampshire, which was not included due to its location in New Hampshire.

Samples were foamed by a pneumatic technique developed by B.C. Research to maximize foam removal (9,10). The ASTM blender technique was replaced with the B.C. Research Technique because the B.C. Technique is more exhaustive, resulting in better foam removals. Also, the B.C. Technique provides essentially the same information as a full scale pilot study at a fraction of the cost. The samples were analyzed before foaming, after foaming, and the collapsed foam was also analyzed. Analysis was performed to detect weakly acidic surfactants (e.g., resin and fatty acids) and strongly acidic surfactants (e.g., polyaromatic pulping products). The latter analysis was conducted by Daniel W. Armstrong, Ph.D., at Georgetown University.

DISCUSSION OF PHASE IV DATA

The Rumford-Mexico and Lewiston-Auburn treatment plant effluents did not produce a collectible quantity of foam when subjected to the pneumatic treatment. Pejepscot Paper Mill treatment plant effluent produced collectible foam only on the fourth day of sampling. Boise Cascade Paper Co., International Paper Co., and Lisbon Falls treatment plant effluents all produced collectible foam on each day. Boise Cascade generated several times as much as the other two, which were roughly equivalent. The four-day averages of collapsed foam volumes in percent of original sample volume were: Boise Cascade: 3.7, International Paper: 1.2, Lisbon Falls: 1.0, and Pejepscot Paper: 0.5. Phase IV data is presented in Table 7.

The water from all point sources contained appreciable amounts of polyaromatic pulping products. Water sources near the pulp, paper, and paper-

TABLE 6. PHASE III DATA

Site/Date	Sample Run Description	C17:0 Recovery (%)	Foam (%)	Resin and Fatty Acids										MBAS		Polyaromatic Pulping Products
				OL	LNOL	LNOLN	PIM	SPIM	IPIM	AB	DAB	Cl-DAB	Cl_2-DAB	SDS*	DBS*	Polyfon H*
FE/10-23	Control (pH 6.8)	67	--	142	53	24	93	62	ND	63	ND	ND	ND	0.6	1.4	>12
	Treatment:															
	pH 6.8		0													
	pH 6.8 + Joy	52	23	472	34	ND	97	ND	ND	73	89	ND	ND	10.8	28.2	205
	pH 6.8 + Na_2SO_4		21													
	pH 6.8 + polyphos		0													
	pH 2.7		6													
	pH 2.7 + Joy		15													
	pH 2.7 + Na_2SO_4		20													
	pH 2.7 + polyphos		3													
	pH 10.0		2													
	pH 10.0 + Joy	62	28	452	87	ND	98	ND	ND	ND	49	ND	ND	8.2	18.6	105
	pH 10.0 + Na_2SO_4		21													
BP/10-23	Control (pH 2.1)	70	--	ND	ND	ND	ND	ND	158	130	ND	178	477	0.2	0.6	75
	Treatment:															
	pH 2.1	48	--	57	12	ND	54	ND	ND	ND	ND	ND	ND			
	pH 2.1 + Joy	13	16	1,812	148	ND	ND	ND	ND	ND	ND	ND	ND	9.0	25.2	400
	pH 2.1 + Na_2SO_4		8													
	pH 2.1 + polyphos		19													
	pH 7.9		11													
	pH 7.9 + Joy	29	19	168	ND	ND	22	ND	ND	44	27	ND	ND	12.2	33.4	375
	pH 7.9 + Na_2SO_4	62	16	57	12	ND	54	ND	ND	ND	ND	ND	ND			
	pH 7.9 + polyphos		3													
	pH 9.5		6													
	pH 9.5 + Joy	22	21	ND	ND	ND	ND	ND	ND	ND	175	ND	ND	11.4	31.2	330
	pH 9.5 + Na_2SO_4		9													
	pH 9.5 + polyphos		6													

TABLE 6. PHASE III DATA - Continued

				Resin and Fatty Acids										MBAS		Polyaromatic Pulping Products
Site/Date	Sample Run Description	C17:0 Recovery (%)	Foam (%)	OL	LNOL	LNOLN	PIM	SPIM	IPIM	AB	DAB	Cl-DAB	Cl_2-DAB	SDS*	DBS*	Polyfon H*
BS/10-23	Control (pH 10.0)	61	--	3,247	3,583	ND	ND	ND	1,726	ND	ND	ND	ND			
	Treatment:															
	pH 10.0	74	5	1,323	1,004	ND	ND	ND	12,350	6,555	4,623	ND	ND			
	pH 10.0 + Joy	96	23	203	70	ND	116	145	627	1,215	2,066	ND	ND			
	pH 10.0 + Na_2SO_4		11	482	116	ND	ND	500	9,230	6,606	4,603	ND	ND			
	pH 10.0 + polyphos		15													
	pH 2.8		5													
	pH 2.8 + Joy	53	10	4,248	5,207	ND	375	ND	6,467	6,718	5,077	ND	370			
	pH 2.8 + Na_2SO_4		19													
	pH 2.8 + polyphos		5													
	pH 6.6 +		11													
	pH 6.6 + Joy	57	23	2,646	4,126	76	147	ND	6,428	5,831	3,415	ND	ND			
	pH 6.6 + Na_2SO_4	91	29	2,157	2,786	35	107	ND	5,492	2,932	3,097	ND	ND			
	pH 6.6 + polyphos		10													
FE/10-24	Control (pH 6.8)	52	--	37	ND	8	ND	ND	ND	ND	20	ND	ND	0.1	0.2	185
	Treatment:															
	pH 6.8		0													
	pH 6.8 + Joy		20													
	pH 6.8 + Na_2SO_4		14													
	pH 6.8 + polyphos		0													
	pH 3.5		6													
	pH 3.5 + Joy		16													
	pH 3.5 + Na_2SO_4		19													
	pH 3.5 + polyphos		5													
	pH 10.1		0													
	pH 10.1 + Joy		27													
	pH 10.1 + Na_2SO_4		14													
	pH 10.1 + polyphos		0													
BP/10-24	Control (pH 2.6)	70	--	264	91	ND	58	40	178	ND	98	ND	ND			
	Treatment:															
	pH 2.6	32	10	37	ND	ND	ND	40	ND	ND	ND	ND	ND			
	pH 2.6 + Joy	13	16	1,812	148	ND	ND	ND	ND	ND	ND	ND	ND			
	pH 2.6 + Na_2SO_4 Unstable Foam		2													

TABLE 6. PHASE III DATA - Continued

Site/Date	Sample Run Description	C17:0 Recovery (%)	Foam (%)	Resin and Fatty Acids										MBAS		Polyaromatic Pulping Products
				OL	LNOL	LNOLN	PIM	SPIM	IPIM	AB	DAB	Cl-DAB	Cl_2-DAB	SDS*	DBS*	Polyfon H*
	pH 2.6 + polyphos		5													
	pH 8.0		5													
	pH 8.0 + Joy		19													
	pH 8.0 + Na_2SO_4		6													
	pH 8.0 + polyphos		13													
	pH 10.7		10													
	pH 10.7 + Na_2SO_4		9													
	pH 10.7 + polyphos		0													
BS/10-24	Control (pH 10.0)	67	--	5,545	7,396	ND	ND	ND	16,200	13,870	8,850	ND	ND	0.6	1.4	>20
	Treatment:															
	pH 10.0	80	3	5,752	7,992	52	ND	ND	21,460	14,400	8,710	ND	ND	0.8	1.8	115
	pH 10.0 + Joy	97	26	263	ND	ND	ND	ND	7,478	ND	3,175	ND	ND	12.8	35.8	125
	pH 10.0 + Na_2SO_4		13													
	pH 10.0 + polyphos		18													
	pH 3.0		10													
	pH 3.0 + Joy		13													
	pH 3.0 + Na_2SO_4	57	13	934	177	ND	ND	673	7,362	5,438	4,179	ND	ND	3.4	8.2	155
	pH 3.0 + polyphos		10													
	pH 6.2		10													
	pH 6.2 + Joy	22	15	887	333	ND	ND	ND	8,842	8,339	4,384	ND	ND	4.2	9.8	155
	pH 6.2 + Na_2SO_4	55	17	3,667	2,917	ND	ND	ND	7,366	7,596	3,768	ND	ND	ND	ND	330
	pH 6.2 + polyphos		13													
BP/BS 10-24	200 ml BP/200 ml BS pH 10.0	70	16	600	465	ND	ND	217	3,496	2,379	1,958	53	ND			
	200 ml BP/100 ml BS pH 10.8	48	8	190	142	ND	ND	ND	2,347	1,644	1,424	192	ND			

TABLE 6. PHASE III DATA - Continued

				Resin and Fatty Acids										MBAS		Polyaromatic Pulping Products
Site/Date	Sample Run Description	C17:0 Recovery (%)	Foam (%)	OL	LNOL	LNOLN	PIM	SPIM	IPIM	AB	DAB	Cl-DAB	Cl_2-DAB	SDS*	DBS*	Polyfon H*
FE/10-25	Control (pH 7.4)	60	--	29	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	>90
	Treatment:															
	pH 7.4 + None		0													
	pH 7.4 + Joy		19													
	pH 7.4 + Na_2SO_4		10													
	pH 7.4 + polyphos		0													
	pH 2.6		6													
	pH 2.6 + Joy		16													
	pH 2.6 + Na_2SO_4		19													
	pH 2.6 + polyphos		6													
	pH 10.9		0													
	pH 10.9 + Joy		10													
	pH 10.9 + polyphos		0													
BP/10-25	Control (pH 2.2)	76	--	ND	ND	ND	16	25	134	46	16	ND	ND	3.8	8.8	>80
	Treatment:															
	pH 2.2		5													
	pH 2.2 + Joy	29	16	76	411	ND	ND	ND	ND	ND	ND	ND	ND	8.8	20.0	290
	pH 2.2 + Na_2SO_4		16													
	pH 2.2 + polyphos		16													
	pH 8.8		11											ND	ND	215
	pH 8.8 + Joy		19													
	pH 8.8 + Na_2SO_4		14													
	pH 8.8 + polyphos	42	10	21	ND	ND	31	ND	63	ND	114	ND	ND			
	pH 10.4	52	19	33	ND	ND	ND	77	ND	ND	ND	ND	ND			
	pH 10.4 + Joy		23													
	pH 10.4 + Na_2SO_4		6													
	pH 10.4 + polyphos		2													
BS/10-25	Control (pH 11)	74	--	8,575	11,694	ND	ND	1,765	22,480	18,850	11,650	ND	ND			
	Treatment:															
	pH 11.0	125	8	4,968	6,400	75	ND	ND	26,310	14,780	9,730	ND	57	3.3	7.0	150
	pH 11.0 + Joy		27													
	pH 11.0 + Na_2SO_4	61	13	3,792	3,298	61	ND	ND	9,736	8,731	5,604	ND	ND			

TABLE 6. PHASE III DATA - Continued

Site/Date	Sample Run Description	C17:0 Recovery (%)	Foam (%)	Resin and Fatty Acids										MBAS		Polyaromatic Pulping Products
				OL	LNOL	LNOLN	PIM	SPIM	IPIM	AB	DAB	Cl-DAB	Cl_2-DAB	SDS*	DBS*	Polyfon H*
	pH 11.0 + polyphos		16													
	pH 3.5		6													
	pH 3.5 + Na_2SO_4		6													
	pH 3.5 + polyphos		8													
	pH 7.5	55	17	2,603	718	ND	260	ND	10,230	ND	4,742	220	ND			
	pH 7.5 + Joy	75	23	472	ND	ND	ND	ND	10,116	9,736	5,188	ND	ND			
	pH 7.5 + polyphos		20													
BP/BS 10/25	200 ml BP/100 ml BS pH 10.0		16													
	200 ml BP/200 ml BS pH 10.0		12													
FE/10-26	Control (pH 7.4)	88	--	100	68	38	ND	ND	ND	ND	ND	ND	ND	ND	ND	75
	Treatment:															
	pH 7.4		0													
	pH 7.4 + Joy		19													
	pH 7.4 + Na_2SO_4		13													
	pH 7.4 + polyphos		0													
	pH 3.5		6													
	pH 3.5 + Joy		8													
	pH 3.5 + Na_2SO_4		16													
	pH 3.5 + polyphos		6													
	pH 10.1		0													
	pH 10.1 + Joy		23													
	pH 10.1 + Na_2SO_4		13													
	pH 10.1 + polyphos		0													
BP/10-26	Control (pH 2.0)	71	--	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	1.6	5.2	>10
	Treatment:															
	pH 2.0	85	10	223	159	ND	89	66	ND	ND	ND	ND	ND	2.4	5.4	370
	pH 2.0 + Joy		14													
	pH 2.0 + Na_2SO_4		13													
	pH 2.0 + polyphos		9													
	pH 6.5		0													
	pH 6.5 + Joy		11													

TABLE 6. PHASE III DATA - Continued

Site/Date	Sample Run Description	C17:0 Recovery (%)	Foam (%)	Resin and Fatty Acids: OL	LNOL	LNOLN	PIM	SPIM	IPIM	AB	DAB	Cl-DAB	Cl_2-DAB	MBAS: SDS*	DBS*	Polyaromatic Pulping Products: Polyfon H*
	pH 6.5 + Na_2SO_4		10													
	pH 6.5 + polyphos		3													
	pH 10.5		5													
	pH 10.5 + Joy		25													
	pH 10.5 + Na_2SO_4		13													
	pH 10.5 + polyphos		6													
BS/10-26	Control (pH 11.2)	57	--	7,170	482	8,487	11,190	ND	ND	18,080	12,680	1,454	ND	3.4	8.2	245
	Treatment:															
	pH 11.2	69	5	2,500	4,012	26	ND	ND	12,430	9,433	4,097	ND	ND	2.2	4.6	170
	pH 11.2 10 Sec. Mixing		3													
	pH 11.2 20 Sec. Mixing		3													
	pH 11.2 + Joy		23													
	pH 11.2 + Na_2SO_4		13													
	pH 11.2 + polyphos	69	16	3,851	2,898	ND	105	ND	14,631	9,297	4,600	ND	ND	ND	ND	255
	pH 2.9		6													
	pH 2.9 + Joy		15													
	pH 2.9 + Na_2SO_4		10													
	pH 2.9 + polyphos		6													
	pH 7.0	83	10	482	116	ND	ND	500	9,230	6,606	4,603	ND	ND	3.2	7.6	240
	pH 7.0 + Joy		9													
	pH 7.0 + Na_2SO_4		16													
	pH 7.0 + polyphos		13													
BP/BS 10-26	200 BP/100 BS pH 10.5		13													
	200 BP/200 BS pH 10.0		17													

TABLE 6. PHASE III DATA - Continued

				Resin and Fatty Acids										MBAS		Polyaromatic Pulping Products
Site/Date	Sample Run Description	C17:0 Recovery (%)	Foam (%)	OL	LNOL	LNOLN	PIM	SPIM	IPIM	AB	DAB	Cl-DAB	Cl_2-DAB	SDS*	DBS*	Polyfon H*
FE/10-27	Control (pH 7.1)	49	--	221	430	ND	ND	ND	ND	84	ND	ND	ND	0.3	0.8	>10
	Treatment:															
	pH 7.1		0													
	pH 7.1 + Joy		19													
	pH 7.1 + Na_2SO_4		13													
	pH 7.1 + polyphos		0													
	pH 3.0		0													
	pH 3.0 + Joy		11													
	pH 3.0 + Na_2SO_4		19													
	pH 3.0 + polyphos		9													
	pH 10.1		0													
	pH 10.1 + Joy		25													
	pH 10.1 + polyphos		0													
BP/10-27	Control (pH 2.5)	91	--	89	66	ND	ND	54	92	79	147	ND	ND	ND	ND	230
	Treatment:															
	pH 2.5	57	10	34	ND	ND	ND	130	ND	50	ND	400	ND	2.2	4.6	240
	pH 2.5 + Joy		13													
	pH 2.5 + Na_2SO_4		13													
	pH 2.5 + polyphos		8													
	pH 6.9		8													
	pH 6.9 + Joy		18													
	pH 6.9 + Na_2SO_4		11													
	pH 6.9 + polyphos		3													
	pH 10.3		10													
	pH 10.3 + Na_2SO_4		9													
	pH 10.3 + polyphos		6													
BS/10-27	Control (pH 10.9)	87	--	947	1,490	7,540	ND	ND	ND	2,513	15,060	ND	ND	2.2	4.6	205
	Treatment:															
	pH 10.9	62	5	2,711	3,807	23	ND	21	13,090	11,960	5,717	ND	ND	2.8	6.0	155
	pH 10.9 + Joy		23													
	pH 10.9 + Na_2SO_4		NR													
	pH 10.9 + polyphos		19													
	pH 2.8	87	11	4,786	4,825	ND	ND	ND	9,864	7,980	4,867	ND	ND			

TABLE 6. PHASE III DATA - Continued

Site/Date	Sample Run Description	C17:0 Recovery (%)	Foam (%)	Resin and Fatty Acids										MBAS		Polyaromatic Pulping Products
				OL	LNOL	LNOLN	PIM	SPIM	IPIM	AB	DAB	Cl-DAB	Cl_2-DAB	SDS*	DBS*	Polyfon H*
	pH 2.8 + Joy		16													
	pH 2.8 + Na_2SO_4		13													
	pH 2.8 + polyphos	17	10	6,073	4,350	ND	ND	ND	13,283	8,586	6,004	ND	ND	ND	ND	165
	pH 6.5		16													
	pH 6.5 + Joy		18													
	pH 6.5 + Na_2SO_4		20													
	pH 6.5 + polyphos		15													
BP/BS 10-27	100 ml BP/100 ml BS pH 10.1	32	20	1,783	491	ND	ND	ND	8,753	8,547	5,305	ND	ND	3.4	8.2	320
	133 ml BP/66 ml BS pH 10.3	76	13	202	120	ND	ND	ND	2,676	2,245	1,617	ND	ND	2.0	4.0	290

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1. All values are in ug/l, except for SDS, DBS, and Polyfon H, which are in mg/l.
2. Percent foam determined by ASTM Method # D3519-76.
3. Abbreviations: polyphos = 2 ml of 1% aqueous sodium hexametaphosphate to 200 ml sample
   - OL = Oleic acid
   - LNOL = Linoleic acid
   - LNOLN = Linolenic acid
   - PIM = Pimaric acid
   - SPIM = Sandaracopimeric acid
   - IPIM = Isopimaric acid
   - AB = Abietic acid
   - DAB = Dehydroabietic acid
   - DCS = Dichlorostearic acid
4. Sample analyses of resin and fatty acids is as described in Appendix A, Materials and Methods.

ND = Not detected
Cl_2-DAB = Dichlorodehydroabietic acid
Cl-DAB = Monochlorodehydroabietic acid
SDS = Sodium dodecyl sulfate
DBS = Dodecylbenzene sulfonate
Polyfon H = Commercial sodium lignosulfonate
Joy = 1 ml of 5% aqueous solution of Joy dishwashing detergent to 200 ml sample
BP = Bleach plant acid sewer
BS = Brownstock washer effluent
FE = Secondary clarifier final effluent
Na_2SO_4 = 20 ml of 2M Na_2SO_4 to 200 ml sample

*Laboratory analysis performed by Daniel W. Armstrong, PhD.

TABLE 7. PHASE IV DATA

				Resin and Fatty Acids										MBAS		Polyaromatic Pulping Products	
Date	Location	Designation	C17:0 Recovery (%)	OL	LNOL	LNOLN	PIM	SPIM	IPIM	AB	DAB	Cl-DAB	Cl_2-DAB	SDS*	DBS*	Polyfon H	Volume of Collapsed Foam (ml)
5/6/80	BC	Control	69	<5	ND	<5	ND	ND	ND	54	ND	55	ND	ND	ND	145	345
5/6/80	BC	Defoamed	88	96	ND	37	55	ND	351	ND	767	22	14	ND	ND	160	
5/6/80	BC	Coll. Foam		NSA	NSA	NSA	NSA	NSA	NSA	NSA	NSA	NSA	NSA	1.4	2.8	95	
5/6/80	IP Jay	Control	77	15	<5	17	44	ND	110	ND	145	ND	ND	ND	ND	160	17
5/6/80	IP Jay	Defoamed	91	22	ND	17	40	ND	128	ND	241	39	12	ND	ND	135	
5/6/80	IP Jay	Coll. Foam		NSA	NSA	NSA	NSA	NSA	NSA	NSA	NSA	NSA	NSA	3.2	7.0	10	
5/6/80	Pejepscot	Control	73	6	ND	ND	11	20	12	11	20	37	13	ND	ND	13	0
5/6/80	Pejepscot	Defoamed	89	ND	ND	11	21	ND	44	ND	133	16	9	ND	ND	8	
5/6/80	R-M	Control	76	ND	ND	<5	15	ND	18	ND	22	5	ND	0.2	0.6	13	0
5/6/80	R-M	Defoamed	69	ND	ND	10	<5	ND	24	ND	42	7	6	ND	ND	18	
5/6/80	L.F.	Control	56	7	ND	18	88	53	42	7	658	160	ND	3.2	7.6	20	32
5/6/80	L.F.	Defoamed	56	18	ND	9	65	43	44	23	93	150	54	ND	ND	33	
5/6/80	L.F.	Coll. Foam		NSA	NSA	NSA	NSA	NSA	NSA	NSA	NSA	NSA	NSA	5	13	20	
5/7/80	BC	Control	38	ND	ND	<5	105	ND	12	ND	32	160	20	ND	ND	150	135
5/7/80	BC	Defoamed	25	ND	ND	39	64	ND	ND	ND	224	ND	ND	ND	ND	125	
5/7/80	BC	Coll. Foam		NSA	NSA	NSA	NSA	NSA	NSA	NSA	NSA	NSA	NSA	ND	ND	80	
5/7/80	IP Jay	Control	62	ND	19	23	47	ND	63	ND	105	13	ND	0.4	0.9	147	95
5/7/80	IP Jay	Defoamed	22	24	ND	ND	15	37	31	37	68	95	30	ND	ND	115	
5/7/80	IP Jay	Coll. Foam		NSA	NSA	NSA	NSA	NSA	NSA	NSA	NSA	NSA	NSA	2.3	5.0	71	
5/7/80	Pejepscot	Control	23	8	ND	11	26	ND	42	35	15	ND	ND	ND	ND	7	
5/7/80	Pejepscot	Control (Dup.)		NSA	NSA	NSA	NSA	NSA	NSA	NSA	NSA	NSA	NSA	0.3	0.7	10	
5/7/80	Pejepscot	Defoamed	26	5	ND	7	<5	ND	24	20	12	17	ND	NSA	NSA	NSA	0

TABLE 7. PHASE IV DATA - Continued

				Resin and Fatty Acids										MBAS		Polyaromatic Pulping Products	
Date	Location	Designation	C17:0 Recovery (%)	OL	LNOL	LNOLN	PIM	SPIM	IPIM	AB	DAB	Cl-DAB	Cl_2-DAB	SDS*	DBS*	Polyfon H	Volume of Collapsed Foam (ml)
5/7/80	L.A.	Control	54	ND	ND	ND	9	12	<5	51	39	181	16	0.2	0.6	13	0
5/7/80	L.A.	Defoamed	65	ND	ND	50	22	ND	117	ND	100	24	19	ND	ND	10	
5/7/80	R-M	Control	49	ND	ND	33	51	ND	78	ND	80	ND	ND	ND	ND	12	0
5/7/80	R-M	Control (Dup.)		NSA	NSA	NSA	NSA	NSA	NSA	NSA	NSA	NSA	NSA	ND	ND	15	
5/7/80	R-M	Defoamed	53	ND	ND	20	101	ND	122	ND	ND	ND	ND	NSA	NSA	NSA	
5/7/80	L.F.	Control	68	<5	ND	ND	<5	<5	15	11	21	95	ND	0.8	1.8	23	39
5/7/80	L.F.	Defoamed	70	ND	ND	17	58	ND	50	ND	209	25	8	ND	ND	21	
5/7/80	L.F.	Coll. Foam		NSA	NSA	NSA	NSA	NSA	NSA	NSA	NSA	NSA	NSA	2.5	6.5	18	
5/8/80	BC	Control	45	ND	9	229	376	ND	1657	ND	141	ND	46	0.8	1.8	97	74
5/8/80	BC	Defoamed	54	<5	65	ND	54	55	ND	ND	976	54	ND	0.1	0.2	80	
5/8/80	BC	Coll. Foam		NSA	NSA	NSA	NSA	NSA	NSA	NSA	NSA	NSA	NSA	3.2	7.6	99	
5/8/80	IP Jay	Control	24	10	<5	11	ND	ND	27	139	7	7	ND	ND	ND	135	49
5/8/80	IP Jay	Defoamed	64	8	ND	ND	ND	ND	<5	53	<5	98	<5	ND	ND	97	
5/8/80	IP Jay	Coll. Foam		NSA	NSA	NSA	NSA	NSA	NSA	NSA	NSA	NSA	NSA	5.0	11.2	101	
5/8/80	Pejepscot	Control	69	6	ND	<5	7	19	10	ND	151	20	13	ND	ND	7	0
5/8/80	Pejepscot	Defoamed	51	<5	<5	7	29	ND	39	34	32	17	ND	0.9	1.9	10	
5/8/80	L.A.	Control	51	ND	ND	ND	ND	15	<5	ND	6	59	ND	0.4	0.9	8	0
5/8/80	L.A.	Defoamed	111	ND	ND	ND	<5	17	<5	48	5	55	ND	ND	ND	8	
5/8/80	R-M	Control	52	ND	23	ND	<5	ND	<5	ND	ND	ND	<5	0.5	1.1	9	0
5/8/80	R-M	Defoamed	26	ND	11	ND	ND	ND	ND	85	67	260	ND	ND	ND	12	
5/8/80	L.F.	Control	81	ND	ND	28	54	ND	47	ND	88	ND	ND	1.6	3.8	18	25
5/8/80	L.F.	Defoamed	55	14	ND	14	ND	24	31	40	57	70	22	ND	ND	25	
5/8/80	L.F.	Coll. Foam		NSA	NSA	NSA	NSA	NSA	NSA	NSA	NSA	NSA	NSA	3.0	8.0	19	
5/9/80	BC	Control	25	7	ND	ND	131	ND	ND	107	14	82	ND	0.8	1.6	69	63
5/9/80	BC	Defoamed	73	9	ND	ND	ND	284	ND	97	<5	98	ND	0.1	0.2	90	
5/9/80	BC	Coll. Foam		NSA	NSA	NSA	NSA	NSA	NSA	NSA	NSA	NSA	NSA	2.6	5.7	55	

TABLE 7. PHASE IV DATA - Continued

Date	Location	Designation	C17:0 Recovery (%)	Resin and Fatty Acids										MBAS		Polyaromatic Pulping Products	Volume of Collapsed Foam (ml)
				OL	LNOL	LNOLN	PIM	SPIM	IPIM	AB	DAB	Cl-DAB	Cl_2-DAB	SDS*	DBS*	Polyfon H	
5/9/80	IP Jay	Control	48	19	<5	6	ND	89	19	65	44	74	14	0.4	0.9	125	
5/9/80	IP Jay	Defoamed												ND	ND	70	43
5/9/80	Pejepscot	Control	92	<5	ND	<5	13	ND	20	11	25	23	10	NSA	NSA	NSA	
5/9/80	Pejepscot	Defoamed	89	5	<5	<5	28	ND	31	11	38	33	9	NSA	NSA	NSA	82
5/9/80	L.A.	Control	69	ND	22	ND	ND	ND	ND	<5	ND	<5	ND	NSA	NSA	NSA	
5/9/80	L.A.	Defoamed	84	ND	ND	<5	11	ND	18	ND	14	ND	ND	NSA	NSA	NSA	0
5/9/80	R-M	Control	85	ND	7	<5	ND	ND	ND	7	7	<5	ND	NSA	NSA	NSA	
5/9/80	R-M	Defoamed															0
5/9/80	L.F.	Control	56	268	15	43	69	6	100	ND	14	ND	ND	NSA	NSA	NSA	
5/9/80	L.F.	Defoamed															
5/9/80	L.F.	Coll. Foam												4.0	9.4	10	66

TABLE 7. PHASE IV DATA - Continued

Date Received	Location	umohs/cm at 25°C	Na^+	Ca^{++}	Fe^{++}	Mg++	pH
5/7/80	Boise Cascade	1,100	280	35	1.6	4.0	7.5
5/7/80	IP Jay	1,450	350	20	0.8	3.0	7.5
5/7/80	Pejepscot	295	20	18	0.8	10.5	5.4
5/7/80	Rumford Mexico	380	70	10	0.2	2.3	7.1
5/7/80	Lisbon Falls	395	50	18	0.6	4.3	7.2
5/8/80	Boise Cascade	1,350	300	39	1.3	3.8	7.2
5/8/80	IP Jay	1,400	330	19	0.7	2.9	7.3
5/8/80	Pejepscot	300	20	18	0.7	10.2	6.3
5/8/80	Lewiston Auburn	500	80	17	0.8	4.3	6.8
5/8/80	Rumford Mexico	420	60	11	0.2	2.5	6.9
5/8/80	Lisbon Falls		50	19	0.5	4.3	6.7
5/9/80	Boise Cascade	1,150	260	29	1.2	3.8	7.0
5/9/80	IP Jay	1,500	330	20	0.8	2.9	6.8
5/9/80	Pejepscot	300	20	20	0.8	9.4	5.8
5/9/80	Lewiston Auburn	500	100	20	2.2	4.7	6.8
5/9/80	Rumford Mexico	405	60	11	0.1	2.4	6.7
5/9/80	Lisbon Falls	345	50	19	0.4	5.0	6.6

1. All values are in ug/l, except SDS, DBS, Polyfon H, Na^+, Ca^{++}, Fe^{++}, and Mg^{++}, which are in mg/l.
2. Abbreviations:

ND = Not detected
NSA = Not selected for analysis
OL = Oleic acid
LNOL = Linoleic acid
PIM = Pimaric acid
SPIM = Sandaracopimaric acid
IPIM = Isopimaric acid
AB = Abietic acid
DAB = Dehydroabietic acid
Cl-DAB = Monochlorodehydroabietic acid
Cl_2-DAB = Dichlorodeydroabietic acid
SDS = Sodium dodecylbenzene sulfonate
DBS = Dodecylbenzene sulfonate
Polyfon H = Commercial sodium lignosulfonate

BC = Boise Cascase, Rumford, ME - final effluent
IP Jay = International Paper Company, Jay, ME - final effluent
Pejepscot = Pejepscot Paper Company, Topsham, ME - final effluent
R-M = Rumford-Mexico, ME - POTW, final effluent
L.F. = Lisbon Falls, ME - POTW, final effluent
L.A. = Lewiston-Auburn, ME - POTW, final effluent

3. Na+, Ca++, Fe++, and Mg++ are in mg/l.

* Laboratory analysis performed by Daniel W. Armstrong, PhD.

board mills (e.g., Boise Cascade and International Paper, Jay) contained approximately 100 mg/l polyaromatic pulping products (range 70 to 160 mg/l). Water from other point sources generally contained an order of magnitude less polyaromatic pulping products (range 7 to 25 mg/l). The foam from all point sources tended to have slightly lower polyaromatic pulping products concentrations than the ambient water. This might indicate that some of this material is more surface active than others (i.e., only the surface active portion would most likely be found in the foam). Again, foam from outside of pulp mill point sources tended to have higher levels of polyaromatic pulping products than foam obtained near other point sources.

Highly variable amounts of MBAS were found in most water samples. The highest concentrations of MBAS were consistently obtained near Lisbon Falls, and to a lesser extent near Boise Cascade. Unlike the polyaromatic pulping products, the MBAS were always concentrated in the foam. Foam levels of MBAS varied from less than 0.1 to 13.0 mg/l (as DBS standard). Except for the Lisbon Falls area, the concentrations of MBAS in the water tended to be less than 1.0 mg/l (as DBS standard) and often less than 0.1 mg/l (as DBS standard). The concentrations of MBAS in foam were usually greater than 1.0 mg/l (as DBS standard).

Exhaustive defoaming removed the MBAS, but had no effect on the polyaromatic pulping products. Where foam could be collected, it was found to be enriched in MBAS. Polyaromatic pulping products were not concentrated in the foam. All samples contained low levels of resin and fatty acids, with one exception, Boise Cascade (5/8/80), which contained somewhat higher levels. The level of resin and fatty acids generally found are too low to draw conclusions regarding the effects of foam removal on their concentrations.

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APPENDIX A
MATERIALS AND METHODS

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MATERIALS AND METHODS

EDWARD C. JORDAN CO., INC., - MATERIALS AND METHODS

Analytical Instrumentation

A gas chromatography system is required to perform the volatile and semi-volatile organic analysis listed below. All weakly acidic surfactant data were acquired on a Perkin Elmer Sigma 1 system.

Chemicals and Supplies

All chemicals used throughout the analytical investigation were of the highest quality available. A sufficient quantity of a single lot of nanograde solvents was purchased at the beginning of the project for all analyses. Resin and fatty acid standards were provided by the National Council for Air and Stream Improvement Inc. (NCASI), Corvallis, Oregon. Chromatographic N-methyl-N'-nitro-N-nitrosoguanidine was purchased from Aldrich Chemical Company, Milwaukee, Wisconsin.

Gas-Chromatographic Procedures

Gas chromatography (GC) was used for analysis of resin and fatty acids. Using a GC coupled with a flame ionization detector, trace concentrations of the compounds of interest could be identified and quantified according to the NCASI protocol.[1] Standards of all compounds to be determined were analyzed to establish the linear range of the system. Retention times were identified from standards for qualitative confirmations; instrument response was correlated with concentration of quantitative calculations. Appropriate field and method blanks were analyzed together with sample extracts to assure the integrity of the results. All sample blanks were free from contamination.

EDWARD C. JORDAN CO., INC. - QUALITY ASSURANCE/QUALITY CONTROL

General

Gas chromatography provides the sensitivity and precision necessary for trace analysis of organic compounds in complex matrices; however, to obtain reliable data an adequate quality assurance/quality control (QA/QC), a program must be followed. QA is a system of independent checks or a supervision of each phase of the analysis from preparation of material through sample collection, work-up, analysis, data interpretation, and reporting. Its function is to assure that sampling and analytical protocols are executed in such a way as to ensure the integrity of the data. QC primarily involves the assignment of a numerical value to the results of the analysis scheme, but not exclusively by analysis of blanks and controls. Two additional major contributions to quality control are method validation and recovery studies, which involve identification of sources of error and quantification of error.

Standards of the highest quality and purity were obtained for identification and quantification of the priority pollutants investigated. During the program, a linearity study, shown in Figures A1 through A7, was conducted on the GC system over the range of concentrations encountered during the analysis program. Stability throughout the analytical program of flame ionization detector (FID) response to several compounds is given in Table 8.

Quality Assurance

Analysis of Standards. The entire GC system was evaluated daily with the analysis of a composite standard which contained all compounds of interest. This composite standard was analyzed with each sample set. The composite standard was stored in the freezer to prevent decomposition of sensitive compounds. The daily composite standard analysis supplied data which: 1) verified the integrity of the chromatographic system; and 2) verified machine sensitivity. The chromatogram of the composite standard was reviewed after analysis; peak shape and resolution of the priority pollutants were assessed visually.

TABLE 8. FID RESPONSE FACTORS
(Area counts/nanogram)

	linoleic acid methyl ester	abietic acid methyl ester	heptadecanoic acid methyl ester
	.336	.219	.318
	.435	.262	.345
	.483	.286	.284
	.394	.233	.312
	.372	.238	.307
	.382	.242	
	.396	.243	
	.394	.242	
Average	.399	.246	.313
Standard Deviation	.044	.020	.022

GC Linearity

Upon completion of the various analytical phases, a study was performed to determine the linearity and response of the GC to several of these compounds of interest.

Semi-volatile Organic Compounds

- abietic acid
- dehydroabietic acid
- dichlorodehydroabietic acid
- isopimaric acid
- linolenic acid
- monochlorodehydroabietic acid
- oleic acid
- pimaric acid
- linoleic acid

Standard mixtures of the test compounds were analyzed according to the NCASI procedure.[1]

Figures A1 to A7 are plots of the integrated peak area vs. nanograms of the compound.

Quality Control. Method blanks were processed with each set of samples analyzed by the analytical protocols. Field blanks were collected at each location and during each sampling period, and analyzed identically to the wastewater samples. Sample blanks were analyzed in accordance with the NCASI protocol. These blank analyses provided the following information: 1) data on clean matrix recoveries; and 2) replicate analyses for precision determinations.

GC/MS Addition Quality Control - Deuterated Internal Standards. Internal standards were selected to represent each compound under investigation. By adding deuterated standards to each sample analyzed by GC/MS, it was possible to assess system performance on a per sample basis. Upon completion of each GC/MS analysis, the total ion currents of the characteristic ions of the internal standards were profiled. The areas of characteristic ions for each internal standard were then integrated and a judgment was made on the integrity of the analysis. The percent recovery of the internal standards indicated the complexity of the sample matrix. Percent recoveries of the internal standards which were added before extraction were calculated as follows:

$$\frac{[C_{IS}]' \times 100}{[C_{IS}]} = \%$$

where $[C_{IS}]$ is the concentration of the internal standard added to the sample and $[C_{IS}]'$ is the concentration of the internal standard analyzed. Low recovery of internal standards and/or unacceptable chromatography signalled possible instrument malfunction or operator error and the analysis was repeated.

Recovery data for the internal standards throughout the analysis program are given in the data tables.

Since no EPA approved methods were in effect for the compounds of interest, an inter-laboratory QC program was initiated. All Phase II samples were analyzed by GC/MS in accordance with the GSRI verification phase protocol. The NCASI[1] GC/FID procedure was used to compare with the GSRI data. Good agreement between the two methods was observed. The NCASI GC/FID procedure was used to analyze all of the remaining samples. The inter-laboratory QC data are presented in Table 9.

GC SEMI-VOLATILE ORGANIC ANALYSIS

Scope and Application

1. This procedure is suitable for GC/FID determination of selected semi-volatile additional compounds which are amenable to organic extraction and gas chromatographic resolution.
2. The following compounds have been determined by this method:

   monochlorodehydroabietic acid
   abietic acid
   linoleic acid
   dehydroabietic acid
   dichlorodehydroabietic acid
   pimaric acid
   isopimaric acid
   linolenic acid
   oleic acid
   sandaracopimaric acid

3. This method is applicable to the determination of these compounds in pulp/paper industrial effluents.
4. The sensitivity of the method is not usually dependent upon the level of interferences, but rather instrumental limitations. The limits of detection of 5 ug/l represent sensitivities that can be achieved in wastewaters under optimum operating conditions.

Summary of Method

1. A one-liter sample of wastewater is acidified to pH 2 and serially extracted with methylene chloride using separatory funnel techniques.

The resulting acid-neutral extract is dried and concentrated to a volume of 1 ml or less, and derivatized with diazomethane. GC conditions are described which allow for the measurement of the compounds in the extract.

Interferences

1. All materials and glassware were demonstrated to be free from interferences under the conditions of the analysis by running method blanks.

TABLE 9. COMPARISON OF METHODS: GSRI VERIFICATION PHASE PROTOCOL/ECJ (NCASI) PROCEDURE

(All data in ug/l, corrected for recovery.)

Sample No.	d_{35} Stearate Recovery (%)	OL	LNOL	LNOLN	PIM	ISOPIM	DHA	AB
13	68	8,400/3,575	6,600/ 7,120	600/60	ND/470	2,760/12,730	1,200/ 4,660	18,000/ 8,040
15	72	21,000/5,560	13,500/10,540	ND/1,520	ND/2,220	5,100/17,600	3,450/ 9,020	25,500/13,960
32	80	10,640/9,230	4,180/10,300	274/140	ND/ND	1,820/11,225	836/ 7,100	12,920/12,050
34	72	8,500/10,120	5,100/16,960	289/2,780	ND/7,920	2,100/25,140	850/10,770	13,260/19,320
53	42	6,000/1,245	2,720/ 1,262	ND/ND	ND/ND	1,270/ 1,370	915/ 1,585	5,150/ 1,960

Reagents

1. Preservatives:
    1.1 Sodium hydroxide - (ACS) 10 N in distilled water.
    1.2 Hydrochloric acid - (ACS).
2. Methylene chloride - Pesticide quality or equivalent.
3. Sodium sulfate - (ACS) granular, anhydrous (purified by heating at 400°C for 4 hrs).
4. Diazomethane - Derivatizing reagant (prepared from N-methyl,N'-nitro-N-nitrosoguanidine [Aldrich]).

Quality Control

1. Standard QA practices were used with this method. Field blanks were collected to validate the sampling, storage, and analysis process. Laboratory blanks were analyzed to validate the integrity of the analysis.
2. The linearity of the system was checked over the range of concentrations commonly encountered in sample analyses. A composite standard in various dilutions was used for GC linearity checks.

Sample Collection, Preservation and Handling

1. Grab samples were collected in glass containers. Conventional sampling practices were followed. Composite samples were collected in refrigerated glass containers in accordance with the requirements of the EPA's screening protocol.[2]
2. The samples were iced or refrigerated from the time of collection until extraction. At the sampling location the glass containers were filled with sample, and the sample pH adjusted to 10, as measured by pH meter, with sodium hydroxide.

Sample Extraction

1. Measure 1 liter of sample using a graduated cylinder into a 2 liter separatory funnel; add the internal standard solution. Adjust the sample pH to 2 with hydrochloric acid.
2. Add 60 ml methylene chloride to the graduated cylinder and rinse. Transfer the rinse solvent and 65 ml more CH_2Cl_2 into the separatory funnel and extract the sample by shaking the funnel for 2 minutes with periodic venting to release vapor pressure. Allow the organic layer to separate from the water phase for a minimum of 10 minutes. Recover methylene chloride layer, and repeat the sample extraction with two additional 50 ml portions of methylene chloride using the same procedure.
3. Combine all fractions of methylene chloride (rinses and extracts). Filter extract through a drying column containing 3-4 inches of anhydrous sodium sulfate, and collect it in a 500 ml Kuderna-Danish (K-D) flask equipped with a 10 ml concentrator tube. Rinse the Erlenmeyer flask and column with 20-30 ml methylene chloride to complete the quantitative transfer.

4. Add 1 to 2 clean boiling chips to the flask and attach a three-ball Synder column. Prewet the Synder column by adding about 1 ml methylene chloride to the top. Place the K-D apparatus in an oil bath so that the concentrator tube is partially immersed in hot oil and the entire lower rounded surface of the flask is bathed in heat. Adjust the vertical position of the apparatus and the oil temperature as required to complete the concentration in 15-20 minutes. When the apparent volume of liquid reaches 1 ml, remove the K-D apparatus and allow it to drain for at least 10 minutes while cooling. Complete concentration with dry nitrogen stream.

GC Analysis

1. The GC conditions are given in Table 10. Inject 5 ug/l of derivatized extract with the oven temperature at 140°C. Hold at 140°C for three minutes then program the GC temperature to rise to 235°C at 2°/min.
2. After the solvent front and excess diazomethane are eluted collect continuous GC data throughout the chromatogram until the last compound of interest has eluted.

Identification and Quantification

1. Identify the compounds of interst in a sample by comparing the GC data of the sample with the GC data of the composite standard analyzed that day. The presence of a compound is confirmed in a sample by the occurrence of a peak at the predicted retention time ± 0.5 min.
2. Report results in ug/l corrected for recovery.

DANIEL W. ARMSTRONG - MATERIALS AND METHODS

Measurement of methylene blue active substances (MBAS) was done by the method of Wang and Langley.[3,4]

Solutions and Reagents

1. Stock linear alkylate sulfonate (LAS) solution: Dodecylbenzenesulfonate, sodium salt, was obtained from Pfaultz & Bauer, Inc. and recrystallized from HPLC grade methanol. 1.000 g of pure LAS was dissolved in distilled water and diluted to 1L.
2. Standard LAS solution: 50.00 ml of stock LAS solution was diluted to 1L with distilled water. Therefore, 1.00 ml of this solution contained 50.0 μg LAS.
3. Buffer solution: 250 ml of 0.5M citric acid and 250 ml of 0.2M disodium hydrogen phosphate were mixed together (distilled water was used for all solutions).

4. Methylene blue reagant: 0.625 grams of methylene blue was added to 400 ml of distilled water. 10.0 ml of concentrated H_2SO_4 was added and the solution was mixed until complete dissolution occurred. The solution was diluted to 500 ml.

Procedure

1. Calibration curve preparation: Seven separatory funnels with 0, 0.50, 1.00, 1.50, 2.00, 2.50, and 3.00 ml of standard LAS solution were prepared. Sufficient distilled water was added to each funnel to bring the volume to 50.0 ml. Each standard was treated as in procedure 2a, b, c and d. A calibration curve of mg/l LAS versus absorbence is made.
2. Anionic surfactant analysis: 50 ml of the water sample is placed into a separatory funnel and treated as follows:
   a. 1.0 ml of methylene blue reagant, 5.0 ml of buffer solution and 25.0 ml of chloroform is added to each separatory funnel. The solution is shaken vigorously for 60 sec. Allow the solution to separate into aqueous and organic layers for 15 minutes.
   b. Separate chloroform from water.
   c. Determine the absorbence of the chloroform solution at 652mm.
   d. Determine the equivalent LAS concentration from the standard curve.

Polyaromatic pulping products were determined by HPLC using a Varian 5020 HPLC unit with a UV_{254} detector and Varian reverse phase, 30cm, MCH, 10μ column. The mobile phase was HPLC grade water and the flow rate was 1.5 cm^3/min.

1. A standard curve of polyfon-H (a commercial lignosulfonate from Westvaco) was made. 10 ul of 1, 5, 10, 20, 50, 100, 150, 200, 300, and 400 mg/l standard polyfon-H solution were injected. The peak area versus polyfon-H concentration was plotted.
2. 10u of the sample was injected. All peaks with retention times between 1.1 min. and 1.6 min. were counted as polyaromatic pulping product substances.[†]*

[†] LAS also elutes in this time frame, however, the concentration of LAS is generally so much smaller than the lignosulfonate-like substances that this error is acceptable.

*Slightly different retention times are a result of many different factors such as: 1) different solution pH's; 2) different molecular weights of the polyaromatic pulping products; and 3) slightly different structures.

TABLE 10. SUMMARY OF ANALYSES

1. Semi-volatile organic analysis by GC

Extraction conditions

1 liter sample (pH = 10)
Adjust pH <2 with concentrated HCl
Spike with heptadecanoic acid (recovery standard)
Serial extraction with dichloromethane (125, 50, 50 ml)
Break emulsions by glass wool filtration
Dry with sodium sulfate
Concentrate sample by Kuderna-Danish evaporation to 1.0 ml

Gas chromatograph - Perkin-Elmer Sigma 1

Column: 5% SP 2330 on 100/120 chromosorb W/AW, 2 mm x 10 ft glass
Flow rate: 30 ml/min
Detector temp: 350°C
Injector temp: 250°C
Temperature program: 140°C for 3 min to 235°C for 5 min at 2°C/min.
Detector: Flame ionization (FID)

2. Semivolatile organic analysis by GC/MS

Extraction conditions

1 liter sample (pH = 10)
Adjust pH <2 with concentrated HCl
Spike with deuterated internal standards
Serial extraction with dichloromethane (125, 50, 50 ml)
Break emulsions by glass wool filtration or solvent addition
Dry with sodium sulfate
Concentrate sample by Kuderna-Danish evaporation to 1.0 ml
Add 100 μg/vial d_{10} anthracene
Store sample in 5.0 ml serum vial with teflon/rubber septum

Mass spectrometer - HP 5985

Amu range: 35-450
Scan speed: 300 amu/sec
A/D per 0.1 amu: 3

TABLE 10. - Continued

Gas chromatograph - HP 5840

Column: SE-30 SCOT (SGE D grade >40,000 Neff)
Flow rate: 22 cm/sec at 200°C
Injection volume: 1 ml, splitless injection
Temperature program: 30°C to 260 at 6°/min

3. Derivatization conditions (trimethylsilyl derivatives)

A. Trimethylsilyl esters (GC/MS)

Place 100 µl sample plus 50 µl MSTFA in conical vial, heat for 15 min. at 70°C, cool to room temperature prior to injection.

B. Methyl esters (GC)

Diazomethane is prepared in diethyl ether from alkalinization of N-methyl-N'-nitro-N-nitrosoguanidine as described in Analytical Chemistry, Volume 45, No. 13, November 1973. Derivatizing reagent is prepared by adding one part methanol to nine parts diazomethane in diethyl ether. Samples containing mg/l levels of resin and fatty acids are extracted and concentrated to 1.0 ml as previously described, and 50 microliters are added to 1.0 ml derivatizing reagent and incubated one hour at room temperature. Samples containing low (0.1 µg/l) levels of resin and fatty acids were extracted and concentrated to near dryness, brought up to 0.3 ml with derivatizing reagent and incubated one hour at room temperature.

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[2] "Sampling and Analysis Procedures for Screening of Industrial Effluents for Priority Pollutants." Environmental Protection Agency, Cincinnati, Ohio, March 1977, revised April 1977.

[3] Wang, L.K. and Langley, D.F. New England Water Works Association, LXXXIX, 4, 301 (1975).

[4] Wang, L.K. and Langley, D.F. Arch. Environ. Contam., 5, 447 (1977).

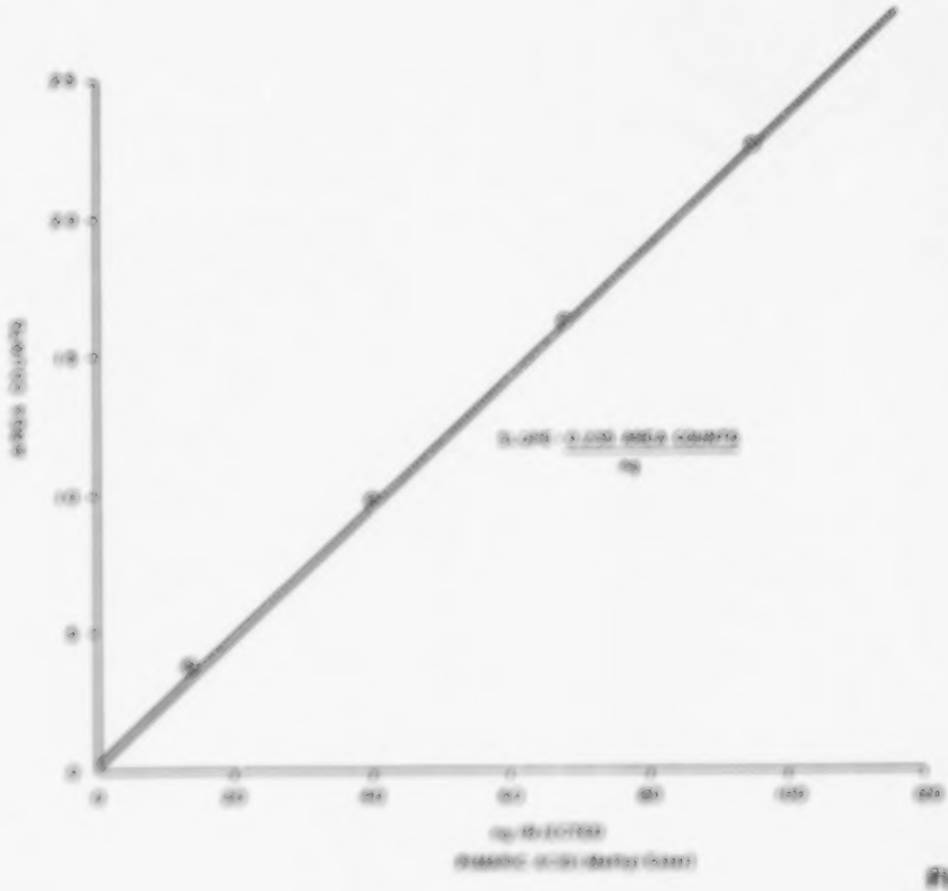

FIGURE 4-1

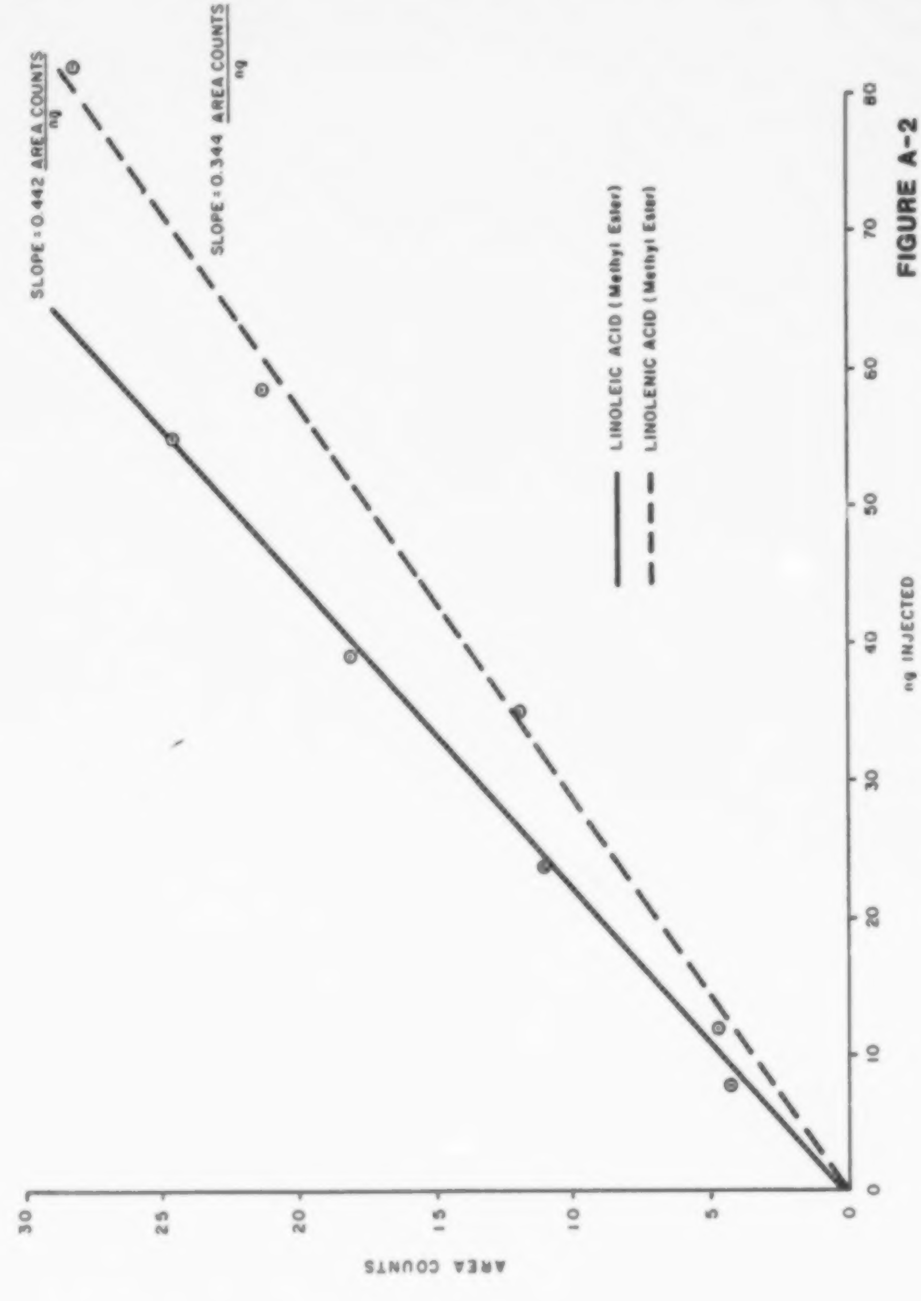
SLOPE = 0.442 AREA COUNTS / ng
SLOPE = 0.344 AREA COUNTS / ng
LINOLEIC ACID (Methyl Ester)
LINOLENIC ACID (Methyl Ester)
AREA COUNTS
0
5
10
15
20
25
30
ng INJECTED
0
10
20
30
40
50
60
70
80

FIGURE A-2

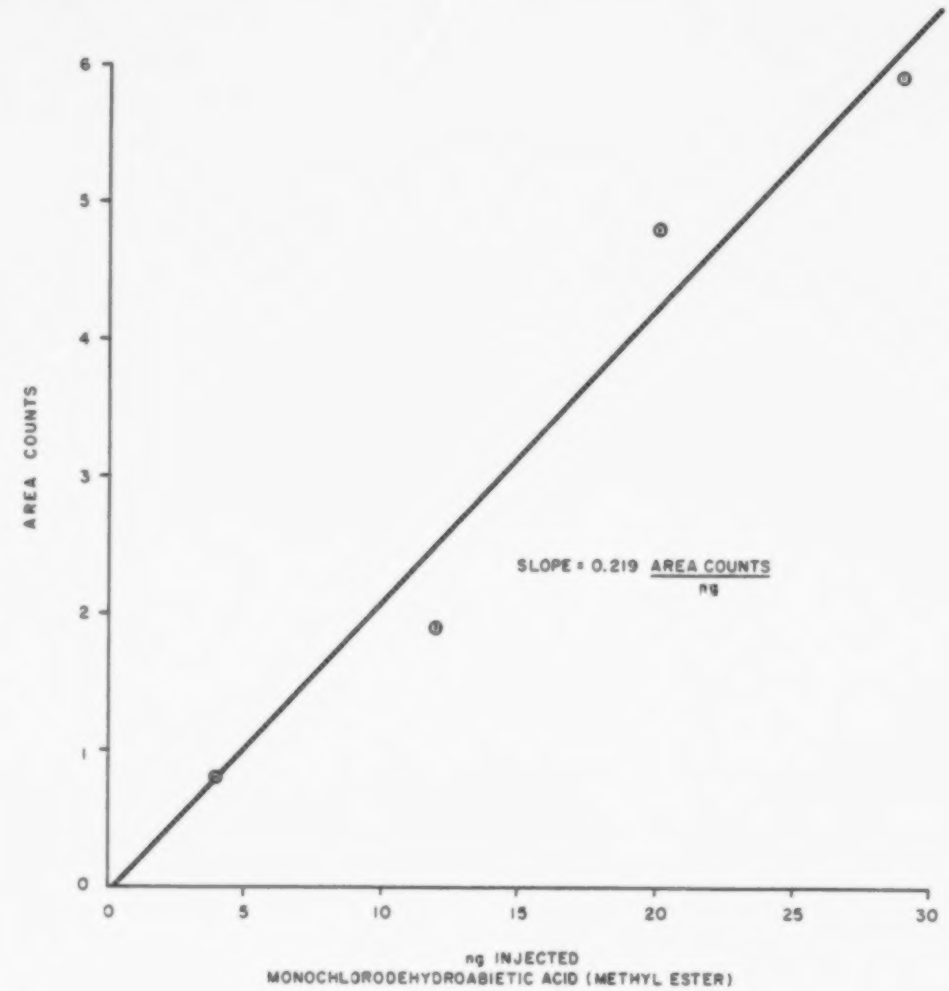
6
5
4
3
2
1
0
AREA COUNTS
0
5
10
15
20
25
30
SLOPE = 0.219 AREA COUNTS / ng
ng INJECTED
MONOCHLORODEHYDROABIETIC ACID (METHYL ESTER)

FIGURE A-3

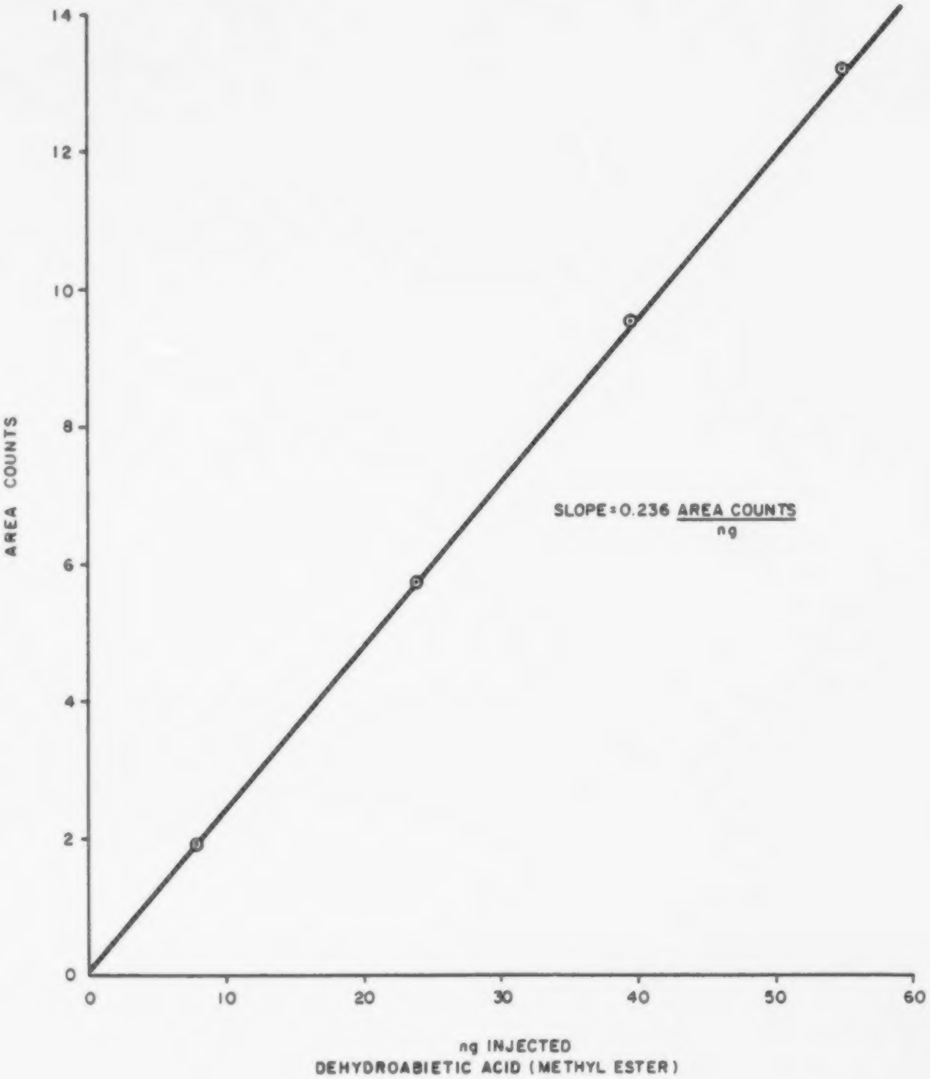
14
12
10
8
6
4
2
0
AREA COUNTS
0
10
20
30
40
50
60
ng INJECTED
DEHYDROABIETIC ACID (METHYL ESTER)
SLOPE = 0.236 AREA COUNTS / ng

FIGURE A-4

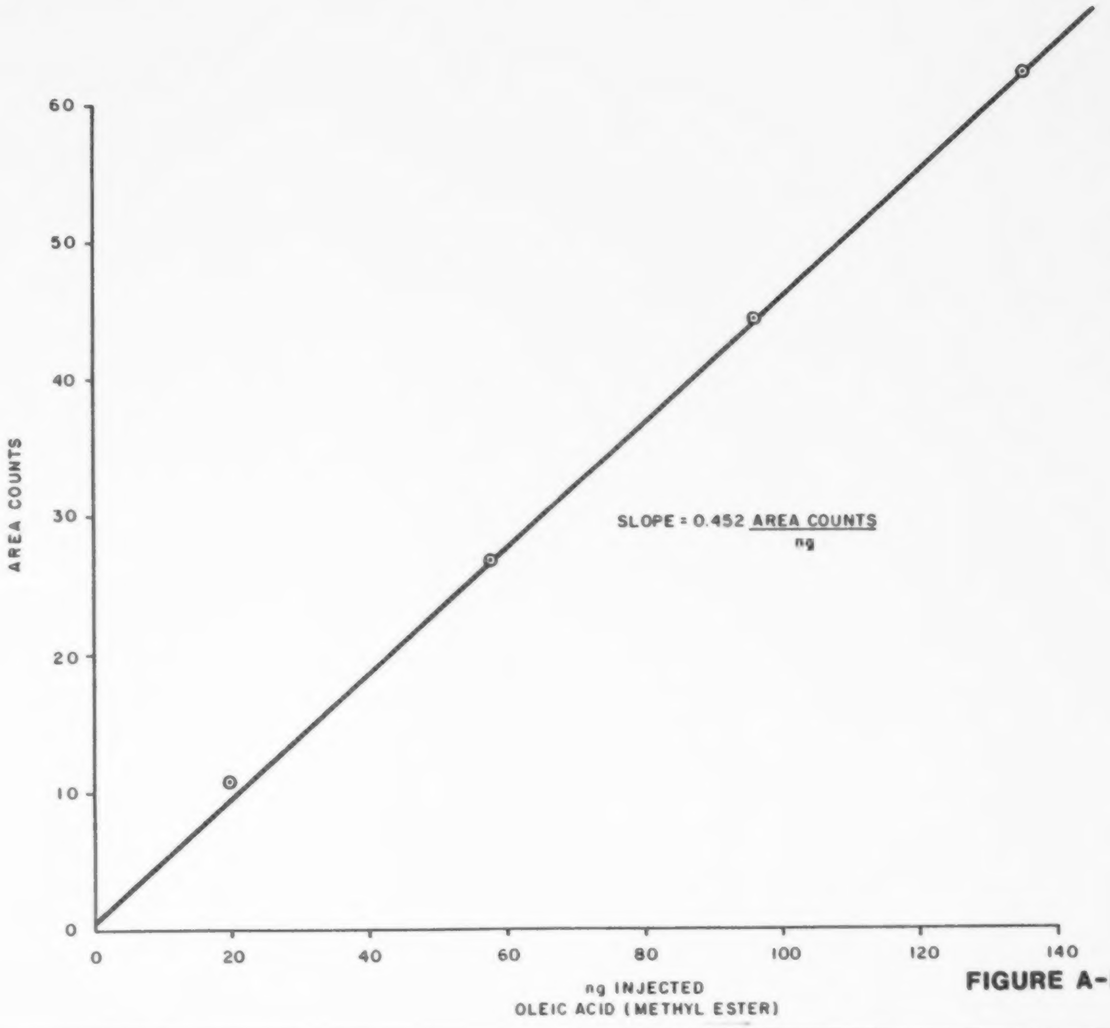
60
50
40
30
20
10
0
AREA COUNTS
0
20
40
60
80
100
120
140
ng INJECTED
OLEIC ACID (METHYL ESTER)
SLOPE = 0.452 AREA COUNTS / ng

FIGURE A-5

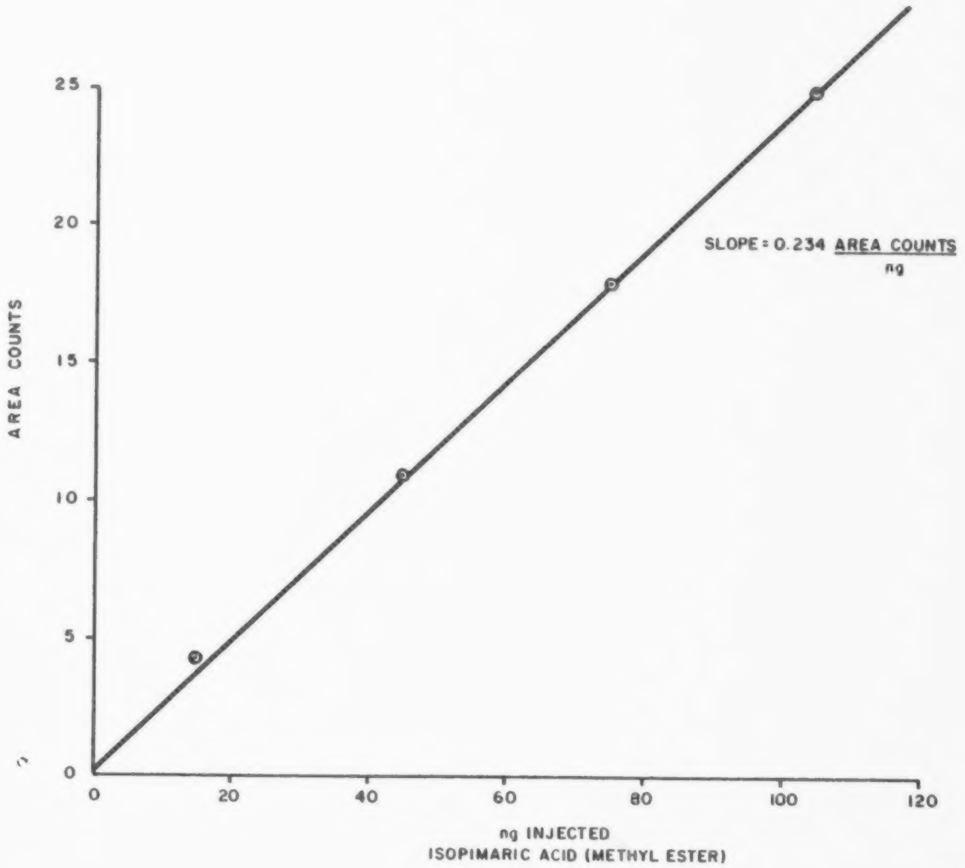
SLOPE = 0.234 AREA COUNTS / ng
AREA COUNTS
0
5
10
15
20
25
0
20
40
60
80
100
120
ng INJECTED
ISOPIMARIC ACID (METHYL ESTER)

FIGURE A-6

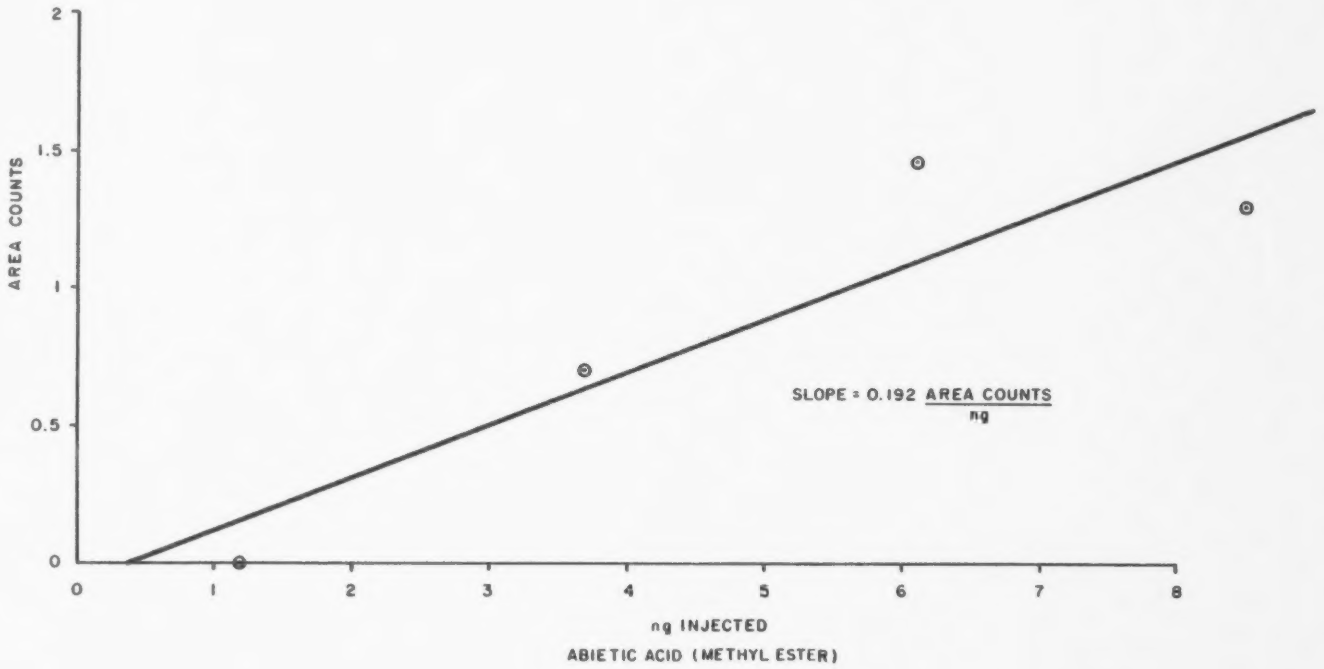
2
1.5
1
0.5
0
AREA COUNTS
0
1
2
3
4
5
6
7
8
ng INJECTED
ABIETIC ACID (METHYL ESTER)
SLOPE = 0.192 AREA COUNTS / ng

FIGURE A-7

APPENDIX B
LITERATURE REVIEW
FOAM AND ITS ELIMINATION

LITERATURE REVIEW

FOAM AND ITS ELIMINATION

February 1979

Prepared by

E.C. Jordan Co., Inc.

Portland, Maine

for the

U.S. Environmental Protection Agency

Project #68-03-2605

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NOTICE

The attached document is the CONTRACTOR'S REPORT. It includes technical information and recommendations submitted by the Contractor to the United States Environmental Protection Agency (EPA) regarding the subject industry. It is being distributed for review and comment only. The report is not an official EPA publication.

The report shall have standing in any EPA proceeding or court proceeding only to the extent that it represents the views of the Contractor who studied the subject industry and prepared the information and recommendations. It cannot be cited, referenced or represented in any respect in any such proceedings as a statement of EPA's views regarding the subject industry.

U.S. Environmental Protection Agency
Industrial Environmental Research Laboratory
Cincinnati, Ohio

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The report was prepared under the direction of Mr. Willard Warren, Project Manager, with overall coordination provided by Mr. Donald R. Cote, Vice President, Environmental Services. Research, review and report preparation were accomplished by Roy L. Walden, Project Engineer, Dr. Bruce Wallin, Robert A. Steeves, Charles Cox and Anne Thompson.

1. SUMMARY

Review of currently published data concerning foam, its causes and control has been accomplished under contract with the U.S. Environmental Protection Agency as Project # 68-03-2605.

Foam is a complex, dynamic system. The variables involved include composition, pH, temperature, method of production and a multitude of physical characteristics dependent on the above. As the system is dynamic, most variables are also time dependent.

The variety of combinations which produce stable foams preclude a blanket policy of control technology. Each system must be individually analyzed. Among those control technologies cited in this review are:

- Mechanical Shear and Impact
- Sonic Disruption
- Orifice Systems
- Heat Treatment
- Dilution
- Changes in Surface Activity and Chemical Potential
- Gamma Irradiation

Mechanical defoaming techniques have several advantages. First, no additional chemicals are added to the waste stream. Mechanical defoaming also allows the use of foam separation processes, yielding significant benefits in detoxification and subsequent treatment of the defoamed waste stream.

Chemical defoaming is beneficial in that foam may be controlled at an intermediate point within the process, greatly aiding process control and thus profitability. Of the chemical defoamants tried, the family of silicone compositions were reported to be the most effective, although higher costs must be considered in any selection.

Mechanical foam breakers of various configurations were reported effective. Conflicting data from similar studies recommended both turbine and plain-basket centrifugal devices.

Continuing studies in the field are being pursued by the E.C. Jordan Co., Portland, Maine, the Maine Department of Environmental Protection and

the National Council of the Paper Industry for Air & Stream Improvement. These groups and the literature indicate that, in order to minimize the variables involved, efforts should be made to develop a consistant generator for single bubble foam.

2. INTRODUCTION

2.1 Background

The rivers of northern New England have, for some time, been noted as being more prone to foam generation than similar rivers in other areas of the United States. Foam is generally considered by the public as being introduced to rivers by industry, mainly from pulp and paper mills. Its high visibility tends to accentuate the adverse public reactions to industrial waste discharges in general, and to the local pulp and paper mills specifically. Although it is also known that several of the foam producing substances occur naturally, and that some rivers produce foam upstream of any industrial discharges, foam elimination has become a priority concern.

This literature review has been prepared under Contract 68-03-2605 from the U.S. Environmental Protection Agency to review and assess current technologies for foam elimination, particularly those applicable to the pulp and paper industry. Literature sources were researched in part by computer program to segregate relevant articles and minimize search time. Articles thus located included international sources as well as current national publications. Abstracts were utilized in cases where the desired source had not been translated into English.

The literature review included the following sources:

Institute of Paper Chemistry

Chemical Abstracts

Chemical Engineering

Chemical Engineering Progress

Environment Canada "WATDOC" Program

Oasis, Pollution Abstracts/Biosis Citation/Orbit III Program

Oasis - Medlars II Program

Selected Water Resources Abstracts Program

Xerox University Microfilm Program

Pulp & Paper

Pulp & Paper, Canada

Tappi

Journal of the Water Pollution Control Federation

National Council of the Paper Industry for Air & Stream
Improvement

Data was also collected from private and industrial sources, as well as from various departments of the governments of the United States and Canada.

2.2 Foam Characteristics

Foam is defined as a two-phase colloidal system, specifically a gas dispersed in a liquid. In this case, the gas is usually air and the liquid water. A pure liquid, however, will not foam. A third agent, termed a surfactant, is also required. Surfactants are molecules exhibiting partial solubility in water; portions of the molecule remain insoluble. This property causes surfactants to concentrate at the gas/liquid interface, thus satisfying both portions of the molecule. In this way, a surface layer is formed which is different in composition from the bulk of the solution.

Figure 3 (3) indicates the orientation of a surfactant molecule (sodium stearate) prior to foaming. The polar portion remains on the water side of the interface while the non-polar, hydrophobic portion extends into the gas phase. Upon foaming, the surface film forms bubbles which retain this configuration, as illustrated in Figure 4 (3).

Bendure (1) reported that the bubbles thus formed range typically between one millimeter and a few centimeters in diameter. Film thickness ranges from a few millimeters in wet foams to only a few thousandths of a millimeter in highly drained foam. Although the bubble begins as a spherical form; as film drainage occurs, a polyhedral shape is assumed for closer packing. The arrangement may be typified as pentagonal dodecahedra.

Foam stability in the two-phase system is related (2) to the specific solution, its ionic character, viscosity, surface tension, temperature, pH, and surfactant concentration, as well as other parameters. Hercules (3)

FIGURE 3
SURFACTANT (SODIUM STEARATE) CHARACTERISTIC(3)

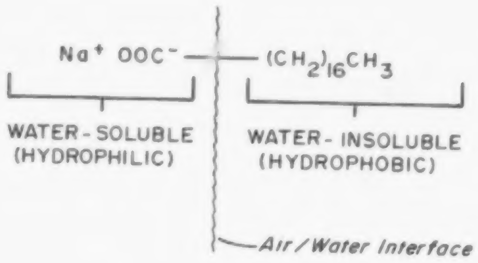
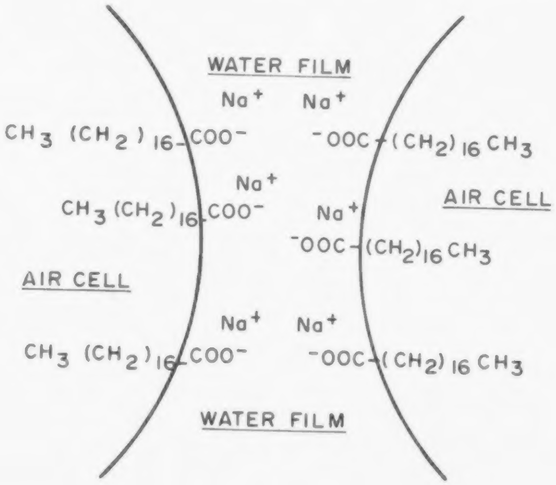

Na⁺ OOC⁻ — (CH₂)₁₆CH₃
WATER-SOLUBLE (HYDROPHILIC)
WATER-INSOLUBLE (HYDROPHOBIC)
Air/Water Interface

FIGURE 4
SURFACTANT ORIENTATION IN FOAM(3)


WATER FILM
Na⁺ Na⁺
CH₃ (CH₂)₁₆ COO⁻
⁻OOC (CH₂)₁₆ CH₃
Na⁺
CH₃ (CH₂)₁₆ COO⁻
Na⁺
AIR CELL
⁻OOC (CH₂)₁₆ CH₃
AIR CELL
Na⁺ Na⁺
CH₃ (CH₂)₁₆ COO⁻
⁻OOC (CH₂)₁₆ CH₃
WATER FILM

reported four major factors contributing to foam stability; relating to Figure 2-2:

1. Electrical Repulsion - Thinning of the film is prevented by the electrical repulsion of the like-charged surfaces. (The ionized carboxyl groups impart a negative charge to each surface.) For the film to break, it must thin down until the walls meet. However, as the walls or surfaces of the film approach each other, as a result of water drainage from the film, strong electrical repulsive forces are set up between the two surfaces. This prevents, or at least slows down their coalescence.

2. High Viscosity - Draining of the film is inhibited by its high viscosity. The carboxyl groups have a high affinity for water molecules and form thick layers of tightly bound water at each surface. One effect of this bound water is an increase in viscosity of the thin film that makes up the bubble wall. Van der Waal's forces and electroviscous effects combine with the thick layers of tightly bound water to cause viscosities of up to 10,000 centipoise.

3. Self-healing Effect - Rupture of the film is retarded due to the ability of a film to heal itself. Any disturbance at the film surface (a falling dust particle or air motion) which displaces the surface molecules tends to crowd these molecules around the disturbance, thereby exposing water which has a higher surface tension. Surfactant molecules will immediately reorient themselves at the point of disturbance, carrying underlying water with them and healing the rupture. (This is referred to as Marangoni transport.)

4. Film Plasticity - Rupture of the film is minimized because of the plasticity of the film. The presence of surfactant molecules at the surface of a film imparts a certain degree of plasticity or elasticity to the film. This property greatly decreases the possibility of rupture when ever-present external forces act on the exposed film.

Bendure essentially agreed with this analysis and added that the electrostatic forces do not become appreciable until film thickness approaches 100 A. However, external forces are claimed to cause film rupture before drainage produces this thin a bubble wall.

Intermittent thin spots on the bubble wall have been noted (3) as being only two molecules thick, yet the bubble does not collapse. This supports the statement concerning fundamental electrostatic forces.

Another phenomenon which occurs as foams become well drained is the formation of large bubbles from an agglomeration of small bubbles. This is an example of gas diffusion, since the pressure inside a small bubble will exceed that inside a larger bubble. This effect tends to de-stabilize the foam as it presents a larger surface area per bubble to external rupturing forces.

A three-phase foam is also common, and is usually more stable than the two-phase system. Here fine solid particles are dispersed in the film, further preventing bubbles from coalescing. This type of foam is prevalent in pulp and paper mill waste waters, stabilized by the presence of fine fibers.

A further variation which produces a stable foam is a mixture of both non-ionic and ionic surfactants which results in interspersing uncharged molecules in the interface between charged groups. This allows closer packing, and thus more film drainage.

The foam produced obviously depends to a great extent on the way in which air is introduced to the system. A large number of small bubbles has a much greater surface area than a few large bubbles. The presence of a surfactant in the solution tends to lower surface tension and encourage the formation of fine bubbles. The lower surface tension allows the formation of a large surface area from the same amount of work introduced to the system (3). Foam stability is again enhanced since the smaller bubbles rise at a slower rate through the solution, allowing more time for the surfactant molecules to orient themselves. This phenomenon of fine bubble formation is likely to occur as acid and alkaline waste streams are combined, liberating CO_2 etc. within the solution. It is also possible for this phenomenon to produce a foamy solution with no indication or evidence of foaming at the surface. Termed non-visible foam, this variation is extremely difficult to control.

It must be recognized that foam is a very complex system and that the above is only a brief description of foam and its tendencies. Several of the references noted contain very comprehensive foam system analyses.

2.3 Definitive Parameters & Analytical Methods

Foam may be characterized by measuring the various physical parameters discussed below. Many of these are time dependent (1,3).

Expansion Ratio	The expansion ratio of a foam is the volume of foam divided by the volume of liquid contained in the foam, V_f/V_L. An expansion ratio of 10 to 100 is typical (1) of draining foams. For a dry, stable foam, the foam volume is roughly equivalent to the volume of gas contained in the foam.
Foam Density	Foam density may be expressed as a function of expansion ratio $\rho f = \rho L \ (V_L/V_f)$ Typical density values range from 0.01 to 0.2 g/ml.
Surface Area	The surface area produced from a given volume of liquid may be approximated by assuming the liquid to form spherical bubbles with a film thickness of h/2. Then $A = 2\ V/h = fVg/d$

where A = surface area
h = separation between bubbles
d = bubble diameter
f = a shape factor = 6 for spheres

This approximation is not valid as foams become well drained and bubbles become polyhedral. A typical wet aqueous foam with an expansion ratio of 10 yields 5000 cm^2/ml liquid. This corresponds to a film thickness of 0.001 cm. Drained foams produce film thicknesses of 100 to 1000 A.

Hercules reports another relation for surface area, A = $\frac{W}{\ }$; where W = work introduced to the system
= surface tension
Assuming constant work input, the surface area will vary inversely with the surface tension.

Solution Viscosity This is an empirical measurement. The apparent viscosity increases with surfactant concentration. Viscosity also increases with expansion ratio. As the expansion ratio increases, and viscosity increases, a drier foam results. These foams are less subject to collapse from shear forces.

Drainage Rate Drainage occurs both from the lamella and Plateau regions of the foam. The Plateau region is the channel formed at the intersection of bubbles. An empirical solution for drainage rates yields

$$V=V_L[1 - (Bt + 1)]^{-1/2}$$

$$\text{and } Q = dv/dt = \frac{BV_L}{2} (Bt + 1)^{-3/2}$$

where V = volume of liquid drained at time t

V_L = volume of liquid originally contained in the foam

B = a constant

B decreases with foam expansion and viscosity increase. Typical values of B range from 0.5 to 2 min^{-1}.

Surface Elasticity This is related to the "self-healing" effect of Marangoni transport. For a two-phase foam $E = 4\tau\ d\mu/dm$ where E = surface elasticity

τ = surface concentration of surfactant
μ = chemical potential of surfactant
m = amount of surfactant per area of film

More generally, Ellerbe (2) noted that Gibbs, in his fundamental foam studies, defined elasticity as
$E = 2A(d\ \ /dA)$
where A = surface area
= surface tension
This indicates that a stable foam will exhibit a readily variable surface tension.

Foaminess or Foaming Tendency

Several tests are currently utilized to define the foam potential of a given solution. These are discussed separately below.

1. ASTM D3519-76 - Blender Test(10) - This test utilizes a common but specific household blender. It is specified for low viscosity aqueous liquids under high-shear. Two hundred milliliters (200 ml) of solution are placed in a blender container and the liquid level measured at 25°C. The solution is blended at 4000 to 13000 rpm for 30 seconds and the foam height measured. The time required for the foam to subside to a 10mm height is also recorded. Maximum foam height equals the total height minus the initial liquid level.

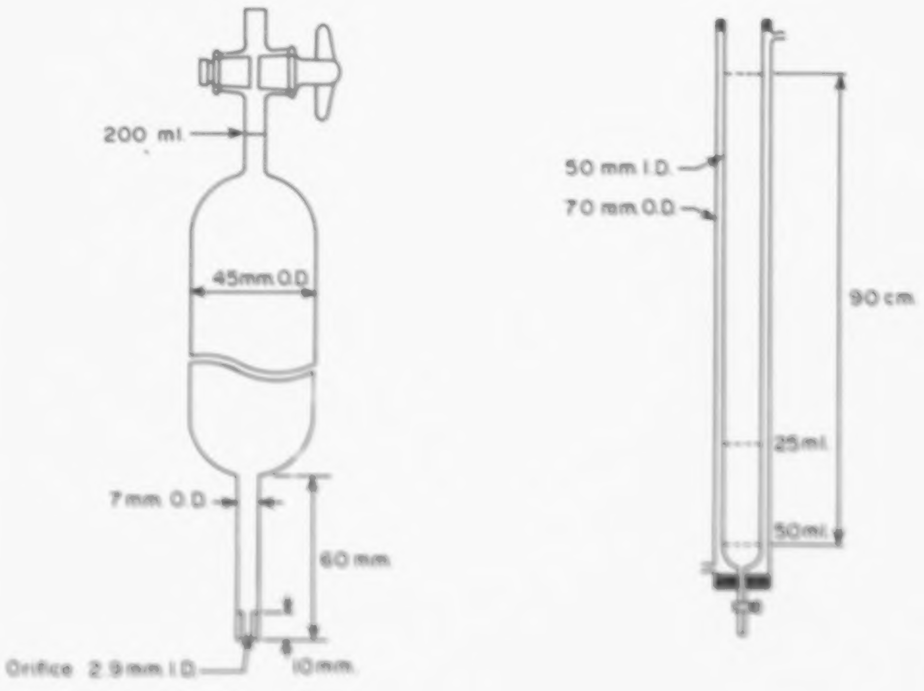
2. ASTM D3601-77 - Bottle Test(10) - This test is specified for low-viscosity aqueous liquids under low-shear. The test apparatus consists of a 16-oz. Boston round bottle or equivalent. Two hundred milliliters (200 ml) of the test solution are placed in the bottle and shaken at 4 strokes per second for ten seconds. The foam height is measured and the time for the foam to subside to a 10mm height is recorded. Calculation is as in ASTM D3519-76.

3. ASTM D1173-53 & 75 - Foaming Properties of Surface Active Agents(10) -
   This method is specified for the determination of the foaming properties of soaps and detergents. The test procedure utilizes a specially constructed glass apparatus as illustrated in Figure 5. Two hundred milliliters of test solution are placed in the foam pipet and 50 ml in the water cooled receiver. The solution is allowed to fall into the receiver. Foam height is recorded after all the solution is in the receiver and again after 5 minutes. The height of the highest average foam height is the desired parameter. This height is stated to be proportional to the volume of air remaining in the foam.

4. BC Research Method - British Columbia Research prepared a project report (11) entitled "Study of Foam Separation as a Means of Detoxifying Bleach Kraft Mill Effluents" in which foaming tendency was defined as:

FIGURE 5

ANALYTICAL APPARATUS - ASTM D1173 (10)


200 ml.
45mm O.D.
7mm O.D.
60 mm.
Orifice 2.9mm I.D.
10mm.
50 mm I.D.
70 mm O.D.
90 cm.
25ml.
50ml.

FOAM PIPET

FOAM RECEIVER

$$\Sigma t = \frac{Vot}{V}$$

where Σt = residence time of an average bubble entrapped in the foam layer
V_o = foam volume immediately after foaming
V = total gas volume utilized
t = time of foaming (in minutes)

This equation is known as the Bikerman Formula (12).

The test consisted of aerating a two liter sample of the test solution for 4 minutes at a gas flow rate of 500 ml/min and measuring the volumetric changes.

5. Ross-Miles Pour Test(1) - This method appears to be a simplified version of ASTM D1173. Two hundred milliliters (200 ml) of the test solution are poured through a standard funnel into a cylinder containing 50 ml of the same solution. Height of the generated foam is measured.

6. Ng & Gutierrez - In their study (6) of mechanical foam breaking systems, influent foaming was defined similar to the previous B.C. Research method. The apparent difference in methods is in volume of sample. A 4 liter sample is aerated at 500 CM^3/min. for 4 minutes.

   Foaming tendency, $t = \frac{\text{Volume of Foam after 4 min. aeration}}{\text{gas flow rate}}$

   Foam stability $s = \frac{\text{Volume of foam after 4 min. settling}}{\text{gas flow rate}}$

7. NCASI - Technical Bulletin 195 (9) specifies use of the Bikerman Formula for reporting foaming tendency. The procedure utilized does not specify a sample volume, aeration occurs at a rate of 200 CM^3/min. for 2 minutes. Foam stability is calculated following 4 minutes of settling. In an effort to standardize results, NCASI then relates the foaming tendency and stability to that of known solutions of alkyl (or dodecyl) benzene sulfonate (ABS). Thus the foam characteristics are expressed in terms of concentrations of ABS.

Ross (13) reported that the majority of the methods utilized to quantify foam properties are inconsistant in that each measures a different complex of properties. Study of a single bubble system was suggested to minimize complications from other factors. Ross goes on to state (14, 15) that measurement of light transmission through foams indicates foam stability. This method also separates the effects of liquid drainage and gas diffusion. Since the method is relatively simple, utilizing a Lumetron colorimeter, rapid evaluation of different antifoaming agents at various concentrations or combinations is possible.

Following his analysis of foam properties, Bendure summarizes the factors which will enhance foam stability as:

> ".increase bulk viscosity
> .increase surface viscosity
> .maintain thick bubble walls, lower the expansion ratio
> .reduce the surface tension
> .increase surface elasticity
> .reduce surfactant adsorption rate
> .prevent evaporation of liquid
> .avoid mechanical stresses
> .eliminate foam inhibitors"

Foam inhibitation or elimination would be pursued utilizing the converse of these statements. Additionally, lowering the pH is reported to decrease foam stability.

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3. IDENTIFICATION OF COMPOUNDS ASSOCIATED WITH FOAMING

Many of the compounds identified in foam are contained in wood(5). The chemistry of wood pulping creates conditions which promote the formation or release of compounds which induce foaming. These naturally occuring or process produced compounds are generalized as:

Resin Acids
Chlorinated Resin Acids
Unsaturated Fatty Acids
Chlorinated Phenolics
Diterpene Alcohols
Diterpene Aldehydes

Easty et al (11) reported the following compounds in pulp mill effluents:

Unsaturated fatty acids:
  Oleic
  Linoleic
  Linolenic

Resin acids:
  Abietic
  Dehydroabietic
  Isopimaric
  Pimaric

Chlorinated resin acids:
  Monochlorodehydroabietic
  Dichlorodehydroabietic

Unsaturated fatty acid derivatives: "Bleach Toxicants"
  9,10-Epoxystearic acid
  9,10-Dichlorostearic acid

Chlorinated phenolics:
  3,4,5-Trichloroguaiacol
  3,4,5,6-Tetrachloroguaiacol

Concentrations of resin and fatty acids were found to range from 0.73 to 28.7 mg/l while "Bleach toxicants" ranged from 0.09 to 1.43 mg/l. Process additives have also been identified as containing surface active agents(6). These additives include:

Resins
Pitch Dispersants
Slimicides
Rosin Size
Dye Stuffs
Wet Strength Additives
Retention Aids
Corrosion Inhibitors
Excess Chemical Defoamers

It has also been noted(1) that many of the compounds found in the pulping process produce large volumes of unstable foam. The presence of lignin and fine fibers tend to stabilize these foams as described in section 2.2 (three-phase foams). However, natural degradation products of lignin (humic acids) occurring in swamp waters failed to foam at concentrations up to 800 ppm (10). This appears consistent with a statement by Holzer (12) that lignin resins exhibit anti-foaming tendencies.

Bruynesteyn(3) reported resin acids at 25 ppm in unbleached white water, 148 ppm in evaporator condensates and 67.5 ppm in a 3% black liquor solution. This report also noted that many of the constituents of contaminated condensates are contained in black liquor, but not the converse. This supports the theory that evaporator foaming is the source of resin acid contamination of condensates.

The woodroom also contributes foam producing compounds. Resin acids were noted at up to 121 mg/l in softwood debarker effluents(8). The major resin acids noted in woodroom effluents were 7,15-isopimaric, abietic and dehydroabietic. Concentrations of the individual resin acids were frequently as high as 20 mg/l. The concentration of resin acids from woodroom operations varied substantially(8) with wood type.

The C-18 fatty acids are reported to have major foam producing properties. Process chemistry may saponify lipids, releasing these acids.

Although contrary to the previous indications that an alkaline state enhanced a stable foam, it was reported(8) that acid bleached effluents will also produce foam upon agitation.

NCASI(7) reported on the foaming potential of various process streams as shown in Table 11.

TABLE 11. TYPICAL "FOAMING POTENTIAL" OF KRAFT MILL EFFLUENTS, ml/liter (7)

Source	"Foam Potential"		
	Pine	Hdwd.	Other
Chlorination washer filtrate	620	670	-
Caustic extraction washer filtrate	1540	1520	-
Calcium hypochlorite washer filtrate (following chlorination directly)	2900	1560	-
Chlorine dioxide washer filtrate	80	80	-
Sodium peroxide washer filtrate	60	-	-
Deckering unbleached stock washer filtrate	-	-	100
Paper machine white water	-	-	10
Dilute black liquor			
750 ppm, total solids	-	-	1540
1500 ppm, total solids	-	-	1520
6300 ppm, total solids	-	-	6670

Very little full-scan constituent analysis has been performed on foam. In general, each researcher analyzed only for those compounds of immediate interest in his effort. In an attempt to provide a broad-based view of foam constituents, research is currently being conducted by the S.D. Warren Co. and the Maine Department of Environmental Protection under an Environmental Protection Agency contract. Assistance is also being provided by the National Council of the Paper Industry for Air and Stream Improvement (NCASI) and various pulp and paper manufacturers. In this effort, samples of receiving waters and collapsed foam are to be analyzed by gas chromatography/mass spectrometry (GC/MS), high pressure liquid chromatography (HPLC), and other techniques in an attempt to quantify the major constituents of foams from rivers receiving pulping effluents.

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4. DEFOAMING TECHNOLOGIES

4.1 General

Breaking of foams may be accomplished by a wide variety of technologies. These include such approaches as:

- .Liquid or air spray impact
- .Mechanical shear & impact
- .Sonic disruption
- .Orifice systems
- .Heat treatment
- .Dilution
- .Changes in surface activity & chemical potential
- .Gamma irradiation

Gaden (21) noted that the incorrect application of the above technologies may actually enhance foam formation. Only thermal methods were cited as free from this possibility. Although not included in Gaden's report, gamma irradiation is not likely to enhance foaming.

The following sections will deal separately with the basic classes of mechanical and chemical defoaming.

It should be noted that removal of the energy source creating the foam would be the simplest and most direct method of foam elimination. This, however, is not always a practical solution.

On the other hand, foam separation yields substantial benefits in detoxifying effluents prior to biological treatment (2,4,5). Thus, allowing/encouraging foaming and then breaking/removing the foam for later treatment may prove to be a better long term goal than foam prevention. This approach reportedly reduces foaming tendency of the effluent by 80%, with about 2% of the total effluent volume being separated. The Georgia Kraft Company (31), however, reported only a maximum 60% reduction in foaming tendency in pilot scale column systems.

4.2 Mechanical Defoaming

Foam separation is one technique reported to detoxify pulp and paper mill effluents. This process, however, is reported to also remove various compounds related to foaming such as lignin, resin acids and unsaturated fatty acids (1,4). As a result, foam separation can also be used as a foam control technique.

Ng and Temoin (2) report that there are four unit operations involved in foam separation: pH control, foam generation, foam breaking, and subsequent collapsed foam treatment. The interaction of each process as discussed in their report, is shown schematically on Figure 6. In assessing foam generation systems, Ng and Temoin evaluated 5 types of conventional aeration devices and selected turbine, helical and jet aerators as being the most promising. As shown on Table 12, they then evaluated each of these for consistency, reliability, and operating costs. The conclusion was that a jet aeration system would be best suited for commercial operation.

The Georgia Kraft Company (31) reported reflux of broken foam to the foam generator to greatly increase the foam volume. At a reflux ratio of four, foam production of over 90% of the feed rate was noted. Gas to liquid ratios were also noted as critical, with a 1.0 to 1.5 SCFM/gallon ratio recommended.

As shown on Table 13, a similar comparison was made of various foam breaking devices. The writers concluded that "the only system which has been installed commercially and that satisfactorily collapses the foam is the turbine - centrifugal system."

In a similar study, however, Tarutin and Nikolaev (18) evaluated five mechanical foam breakers including disc and paddle turbines and centrifugal devices. Their results indicated plain-wall centrifugal devices to be most efficient. Experiments found foam to be completely broken at a basket speed of 1860 RPM.

Ng also worked with Gutierrez to define the principles of mechanical foam breaking with turbines (3). As a result of their work, they determined that:

1. "Turbine systems can effectively and reliably break foams from kraft mill effluents."

2. Three bladed disc turbines were the optimum foam breaking configuration.

3. Liquid withdrawal type separation systems were much more effective breaking foam than equivalent single flow through systems.

4. Foam breaking efficiency is affected by turbine size, rotation speed, tip velocity and foam flow.

5. A system's foam breaking capacity is approximately equal to (2.6×10^{-3}) x (rotation speed) + (7.7×10^{-2}) x (turbine dia.) - 4.7. Units are rpm and cm.

FIGURE 6
FOAM SEPARATION PROCESS SCHEMATIC (2)

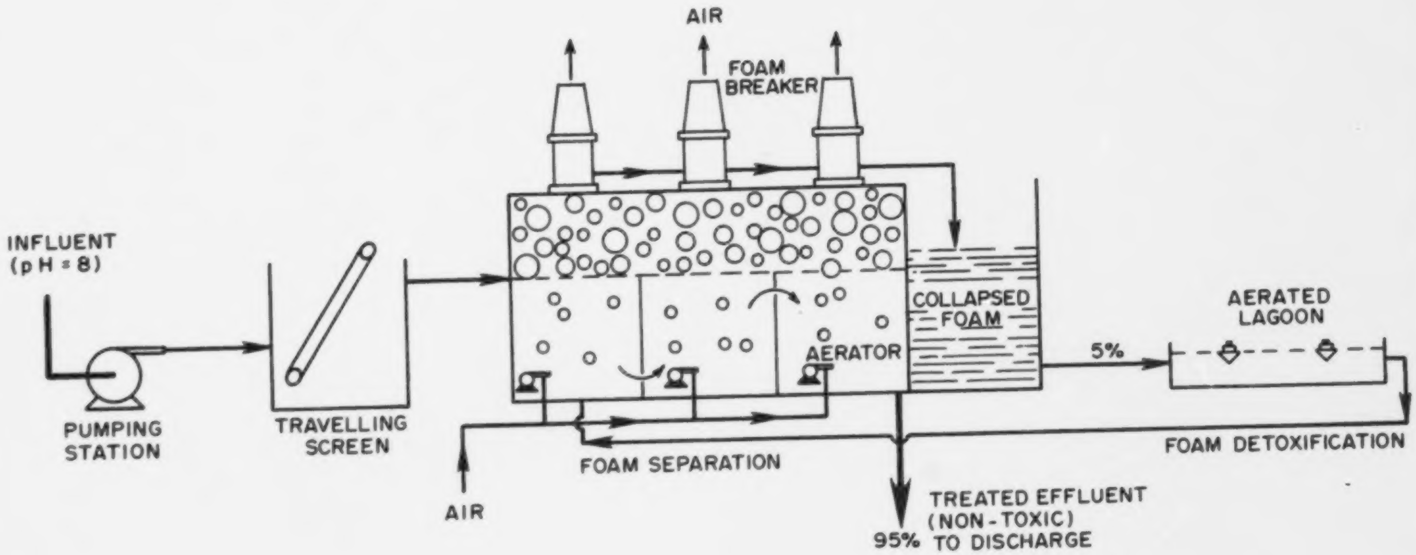

AIR
FOAM BREAKER
INFLUENT (pH = 8)
PUMPING STATION
TRAVELLING SCREEN
AERATOR
COLLAPSED FOAM
AERATED LAGOON
5%
AIR
FOAM SEPARATION
FOAM DETOXIFICATION
TREATED EFFLUENT (NON-TOXIC) 95% TO DISCHARGE

TABLE 12. COMPARISON OF MOST PROMISING FOAM GENERATING EQUIPMENT (2)

Operating Characteristics	Turbine Aerator	Modified helical Aerator	Jet Aerator
CONSISTENCY			
Probability of producing 1 mm bubble diameter	>50%	<50%	>80%
Verification of bubble size	Laboratory experiment	-	Demonstration of working model
Possibility of producing >1 mm diameter bubbles due to poor performance	Slightly possible	Highly possible	Slightly possible
Consequence of producing <1 mm diameter bubbles	Increase aeration rate	Increase the # of aerators & aeration rate	Increase aeration rate
RELIABILITY			
Simplicity of system	More sophisticated	Simple	Simple
Ease of operation	Easy	Easy	Easy
Possibility of breakdown	Highly possible	Minimal	Minimal
Maintenance required	On gearbox, bearing & motor	Minimal	On pump
Possibility of Corrosion	On all mechanical components	None	On pump
ECONOMY OF FOAM GENERATING			
Equipment (25 MGD plant) *Capital cost ($)	375,000	250,000	550,000
hp required	4130	680	1328
*Operating cost ($/ton of pulp)	0.49	0.21	0.42

*Estimated in 1975

TABLE 13. COMPARISON OF VARIOUS FOAM BREAKING DEVICES (2)

Foam breaking System	Operating Principle	Commercial Installation	Practicability for Pulp Mill Application
Air	Impact force, evaporation	None	Impractical
Sonic Pressure	Various acoustic pressures	None	Impractical
Thermal	Evaporation, chemical degradation	None	Impractical
Orifice	Sudden pressure change	None	Impractical
Liquid Spray	Impact force, dilution	Yes	Impractical
Mechanical forces -Whirling paddle		None	Impractical
-Centrifugal/ Turbine	Shear, impact, compression and tension forces	Fermentation industry and pulp & paper industry	Suitable

6. The power consumption of a foam breaking system is approximately equal to [foam breaking capacity] x [$(51.7 \times 10^{-17}) \times (\text{rotation speed})^3 \times (\text{turbine dia.})^5$]. Units are rpm and cm.

Ng and Temoin (2) also evaluated the economies of foam separation by preparing capital and operating cost estimates for a facility capable of detoxifying a flow of 25 mgd from a 750 tpd mill. The results of this evaluation are shown on Tables 14 and 15. All costs are based on 1975 prices.

The conclusions of other researchers concerning foam separation are similar to those presented above (4,5). Mueller, Walden and Ng(4), for example, stated that foam separation can be used by the entire bleached kraft industry. They also report an 83 percent detoxification success rate for the 10 mills studied. It is interesting to note, however, that these researchers found whole mill effluent to be the most easily treated by foam separation. This was felt to be a result of poor foaming characteristics of the individual streams as well as impractical chemical requirements for pH adjustment. A pH of 7 or higher was found necessary for reliable detoxification by foam separation.

Another interesting aspect of Mueller, Walden and Ng's (4) work was their finding that the Dissolved Air Flotation (DAF) process successfully removed both toxicity and suspended solids. They also noted that it was as simple, reliable and trouble free as the previously discussed turbine separation system. Detoxification costs for a 750 tpd mill treating 25 mgd of effluent were estimated as:

TABLE 14. CAPITAL COST (1975) FOR A 25 mgd FOAM SEPARATION PLANT (2)

Process Elements	Installed Cost
pH control	$ 200,000
Pumping station	500,000
Foam separation	
Foam separation tank c/w cover	600,000
Jet aerators c/w blowers	550,000
Foam treatment	
Foam breakers	145,000
3 day aerated lagoon	300,000
Total capital cost	$2,295,000

TABLE 15. ESTIMATION OF OPERATING COST (1975) FOR A 25 mgd FOAM SEPARATION PLANT (2)

			$/Day
Plant cost		$2,295,000	
Capital with 15 years life			
Capital recovery factor	13.5%		
Taxes and insurance	3.0%		
	16.5%		1.0375
Power cost			
Pumping	108 hp	(3)	
Foam separation	1328 hp		
Foam breaking	540 hp		
Biological foam treatment	117 hp	(3)	
Total	2093 hp		374.2
Chemicals 1.1¢/1000 gal.(3)			303.0
Maintenance (5% of capital)			51.9
Labor (include overhead) 4h/day at $16h			64.0
		Total	$1.830.6
		or $2.44/ton of pulp	

Foam Separation System	Capital Cost ($ million)	Operating Cost $/1,000 gal.	
		$/1,000 gal.	$/ton
Porous media	1.12	6.3	2.10
Turbine	1.01	5.3	1.78
Dissolved Air Flotation	1.66	8.1	2.71

Baicheva (1) also worked with pressure flotation and found that lignin, as well as other surfactants, could be effectively removed by this process. Based on his laboratory work, he recommended that flotation take place at 4 atmospheres pressure. A coagulant, aluminum sulfate, should also be added, with the amount depending on the effluent lignin content. The reported advantages with this process are:

1. It decolorizes as well as detoxifies the waste.
2. It doesn't add chemicals which would increase water pollution or prevent effluent recycling.

Much more simple foam breaking devices have been shown effective for certain applications. Stevens (30), for example, reported that a seive located within piping will successfully break foams forced through the pipe under moderate air pressure.

Ultrasonic foam breaking has been studied in some detail. Hay & Shapland (14) reported successful destruction of foams with mean bubble radii from 0.5 to 5mm with a 20-20,000 Hz acoustic source. Boucher (13) reported both high and low frequency (0.7 to 29kc) sound effective but noted a dependency on vessel size. High intensity sound at 12,000 cps from sonic vortex transducers was reported (15) to collapse black liquor foams at up to 1,000 cu. ft./minute. Black liquor foam destruction was also studied by Genev and Grabovski (16) using an aerodynamic or 'siren' type ultrasonic generator. At 31,000 Hz, static foam was reported to be rapidly disintegrated. Under dynamic, flow-through conditions, a considerably slower foam collapse rate was noted. The authors attributed this to the intensity of ultrasound produced by the generator and concluded that industrial foam control by ultrasound was feasible assuming a sufficiently powerful source.

Abrupt pressure changes have also been shown effective in foam collapse. Herzhoff et al (17) have patented a device utilizing both an orifice system and centrifugal separator. The orifice system is contained in a tube with a length/diameter ratio of 20 to 30. Within the tube, at least 3 throttling restrictions with length/diameter ratios of 1.5 to 5 are provided. Collapsed foam is routed to the centrifugal unit for further separation of liquid and vapor phases.

4.3 CHEMICAL DEFOAMERS

Chemical defoamers, compounds added to an effluent stream to control foaminess, often function by coalescing bubbles rapidly (26), causing the formation of large unstable bubbles. Pattle (22) reports that antifoams function by displacement of the surfactant surface layer or, in the case of salt solutions, by preventing negative absorption. Spreading efficiency is stated to exhibit a high correlation with foam killing. Ross (28) determined that defoamants functioned through two mechanisms, or a combination of the two. Some agents were found to promote drainage rates, possibly due to decreased surface viscosity. Other agents actually cause rupture of thick films before drainage can thin the films to the breaking point.

Defoamants are generally characterized by low surface tension, high surface activity, low elasticity, generally low solubility, and high "spreading" efficiency. Compounds utilized as defoamers include petroleum fractions, oils, polymerized glycols and ethers, higher fatty-acid amides and esters, alkyl lactates, organic phosphates and various silicone formulations (6,7,8,9). Another facet of defoamant composition was noted by several researchers. Apparently, the same classes of compounds which cause foaming (resin acids, fatty acids, etc.) may be combined with a wide variety of compounds to produce a defoamant. Louden (29) contains many references to this. The silicone formulations, however, were found to be the most effective(9). An average application would use about 10 mg/l with the normal use range from 2 to 15 mg/l. Emergency control measures often reach dosages as high as 100 mg/l.(8) Dosages of this magnitude, however, may lead to the development of residues, deposited at locations of high shear. These residues may reach a point where pulp contamination occurs.(7) Additionally, excess defoamer may actually cause foam. Kennedy (23) reported that even octyl alcohol, widely used as a defoamant, will generate foam at high concentrations.

To minimize the problems related to overdosing, Ellerbe(7) recommended a two-pump defoamant system as shown in Figure 7. The first pump operates continuously at the minimum rate required for normal operating conditions. A conductivity probe at the foam control point (in this case a washer vat) detects a rising foam level, which activates the second, high rate defoamer pump until the foam level decreases.

The point of addition of chemical defoamers is also an important consideration. Defoamant must be added to the point of air introduction, entrainment, etc. At this point, a minimum amount of surfactant will have penetrated the air/water interface(8). Thus, the defoamant has maximum opportunity to be effective.

Several methods have been published by which a number of defoamants may be compared for efficiency. Hollaender (25) detailed a simple laboratory test. The procedure involves the actual solution causing foam problems, rosin size and alum, to which one drop of the antifoam agent is added. This is repeated with shaking between each drop added until no foam remains. A comparison of the volume of antifoam agents required indicates the most suitable agent for the particular application.

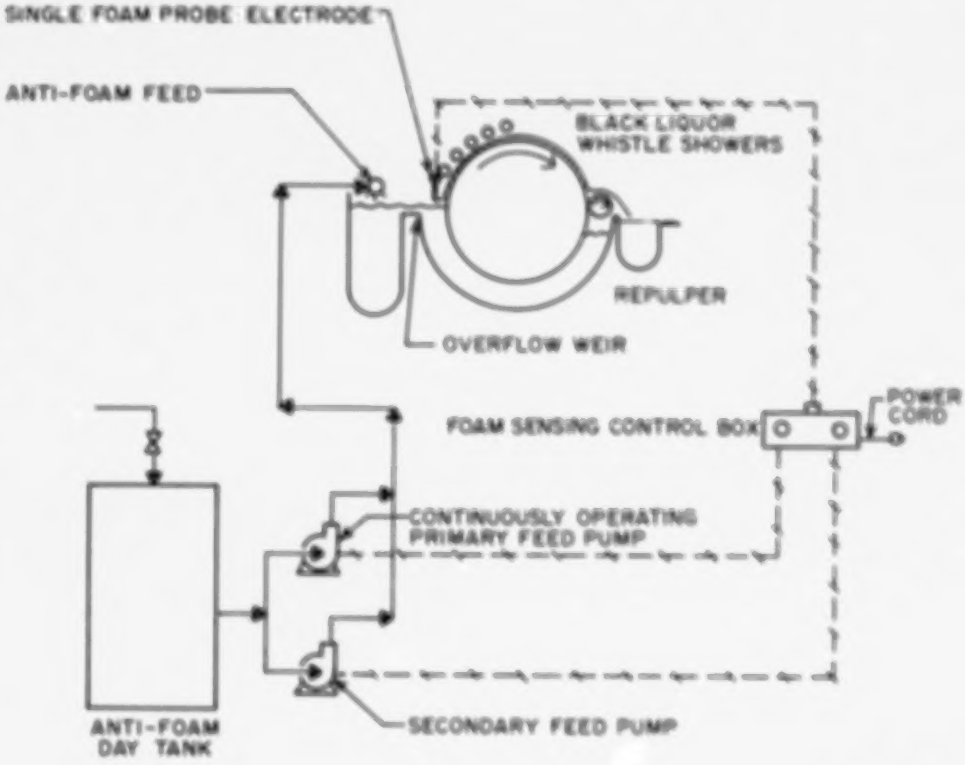
Robinson (26) recommended a method based on the surface tensions of the liquid to be defoamed and of the additive saturated with that liquid. The method allows calculation of a "rupture coefficient." A high positive rupture coefficient is characteristic of high foam inhibiting additives while a negative coefficient indicates no foam reducing properties.

Color removal is also reported to reduce foaming tendency if alkaline black liquor is present. This apparently is due to lignin removal. Both activated carbon and massive lime treatments are noted as color removal techniques. Lignin is associated with both color and foaming tendency.(9)

Dilution of effluents reduces foaming tendency as surfactant concentrations are subsequently reduced. This approach appears to require a 4:1 to 8:1 dilution ratio, based on data that a 50 to 100 mg/l lignin concentration in effluents will not produce a persistent foam in fresh receiving waters.(9) It was also noted that this conclusion assumes the absence of natural organic surface active materials. In the case of ocean discharge,

FIGURE 7

AUTOMATIC ANTI-FOAM CONTROL SYSTEM(7)


SINGLE FOAM PROBE ELECTRODE
ANTI-FOAM FEED
BLACK LIQUOR
WHISTLE SHOWERS
REPULPER
OVERFLOW WEIR
FOAM SENSING CONTROL BOX
POWER
CORD
CONTINUOUSLY OPERATING
PRIMARY FEED PUMP
SECONDARY FEED PUMP
ANTI-FOAM
DAY TANK

salinity must be considered. A 75% seawater solution (approximately 13,000 mg/l Cl^-) effectively doubled the foaming tendency of effluents, whereas normal seawater salinity (at 17,500 ppm) did not increase the foaming tendency further. The dissolved solids in seawater were felt to alter the interfacial properties.(9)

Removal of surfactants by precipitation was studied by Nagasawa(10). Solutions of various surfactants were prepared at 1% concentrations. Organic compounds containing phenolic hydroxyl groups and a flocculant were added, agitated and settled for one hour. Surfactant concentrations in the supernatant were reported at less than 0.05%, yielding 95% removal.

Removal of surfactants by absorption will also decrease foaming tendency. The Rohm and Haas Company (24) has developed a polymeric absorbent in the form of an insoluble crosslinked styrene polymer with macroreticular physical porosity. This absorbent, Amberlite XAD-2, is claimed to remove anionic surfactants (e.g., sodium alkyl benzene sulfonate) at a level of 99%. Nonionic surfactants were absorbed at a 97.5% level but required a 24 hour contact time. Cationic surfactants (e.g., dimethyl benzyl alkyl ammonium chloride) were less amenable to absorption, reaching a 30% removal after 24 hours.

Foam is also reportedly destroyed by irradiation(11). In the noted experiments, fractionated foam was irradiated by accelerated electrons. The process is stated to be effective for industrial wastewaters with high surfactant concentrations. In a related study, Makarochkina(12) compared radiation sources for foam destruction. Three sources; cobalt isotopes, radiation circuits, and electron accelerators were evaluated. Radiation circuits were found to offer economic advantages.

Treatment of foams with heat and solvents is mentioned by Bendure(6) without further note. Gastrock and Reid (19) report that at laboratory scale, heat may be utilized to prevent foaming during concentration of noninflammable liquors. The method employed consists of a helix of nichrome wire suspended in a flask above the liquid being concentrated. For a 2 liter flask, 88cm of Number 22 (gage) wire is specified. Westermeier (20) reported that foam may be removed by heating the foam zone via electrical resistance wires or by injection of hot gases. In the case of an electrically conductive foam, positioning of two electrodes in the foam zone is claimed effective.

Sahlberg (27) reported that treatment of a separated foam with an inorganic acid (e.g., HCl) will break the foam. The acid may be applied in gaseous form.

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4.4 INTERNAL PROCESS MODIFICATIONS

Implementation of internal process controls and/or modifications represents another approach to controlling the pulp and paper industry's foam problem. Examples of potential control measures include the following:

- Use of seasoned wood for pulping
- Improving Brown Stock Washer Efficiency
- Controlling the Use of Chemical Additives and Clean-up Detergents
- Controlling liquid/foam pullover into the digester gas relief system
- Improving Soap Recovery
- Modifying In-Plant Liquid and Stock Handling Procedures
- Reducing Paper Machine Air Entrainment in Stock Streams

Several researchers have found that seasoning effectively reduces the foaming tendency of certain wood species. Green (1), et.al., for example, worked with jack pine sawdust in the laboratory and found that seasoning definitely decreases foaming. Reid (2) reached a similar conclusion from his work with Pinus radiata pulpwood grown in Myora, South Australia. Blackerby (3) surveyed numerous western mills using outside chip storage and found at least one that also reported reduced foaming during pulp processing when seasoned chips are used.

Ellerbe (9) reported that fatty acids in wood are generally saponified to soaps (surfactants) during cooking. After leaving the digester, these soaps form a film at the liquid surface. All that is then needed to cause foaming is agitation of the liquid in the presence of air. The brownstock washers, knotters, and deckers provide just such an action (5,9). It should be noted that black liquor alone contains surfactants and hence causes foaming (5, 11). If washers are overloaded or operated at less than maximum efficiency, these cooking liquors will be carried through the mill to possibly cause foaming problems elsewhere.

There are numerous ways to improve the efficiency of brown stock washers and deckers. One obvious method would be to not exceed the unit's design capacity. Unfortunately, the economics of pulp and paper mill operations are such that this is seldom the case. The advantages of increased production normally more than outweigh the cost of wasted chemicals. A more generally accepted method is to maximize reuse of decker filtrate for stock washing and thereby reduce black liquor losses. This goes hand in hand with closing up the liquid portion of the screen room since decker filtrate can also be used to dilute the brownstock prior to screening and/or centricleaning. There are also several modifications to the countercurrent washing process which can improve washer efficiency and thus reduce foaming problems. Both Bushmelev et. al. (12) and Zimmerman et. al. (13) report that washing kraft pulp in a closed vessel with overpressure effectively accomplishes this. Burling et. al. (14) on the other hand, reports that horizontal foraminous filters in which the residual liquor is removed by vacuum avoids a foaming problem.

Ellerbe (9) reports on several other foam control methods which have been used in the past with success. Unplugging whistle showers, for example, is reported to reduce spray velocity which in turn minimizes pulling air through the pulp mat and subsequent foaming. Revising the shower nozzle orientation will similarly prevent the spray from digging into the mat. Ellerbe also reports that running vat consistencies at the recommended 1 percent level will improve sheet formation on the washer drum and thus help reduce foaming.

The type of washing equipment also affects stock washing efficiency; as evidenced by the experiences of Morgan (8) at the Crestbrook Kraft mill in Skookumchuck, B.C. The Crestbrook facility uses a combination of Kamyr ring type diffusion washers and true diffusion washing in the bottom section of a Kamyr continuous digester as shown on Figure 8. This operation is reported as being extremely successful in reducing soda loss, effluent BOD, and defoamant usage. Soda losses at the plant's 500 adt/day operating rate were reported as 15 to 20 lbs/adtp. This includes both chemically bound and washable soda. Morgan attributes the plant's success to more effective liquor removal with digester diffusion washing due to long detention times and high temperatures. Morgan also noted that outlet pulp consistency has a significant effect on the efficiency of external washers as shown on Figures 9 and 10.

Numerous chemical additives are known to reduce surface tension and thereby promote foaming. Examples of such additives are:

- Resins
- Pitch Control Agents
- Slimicides
- Rosin Size
- Dye Stuffs
- Wet Strength Additives
- Retention Aids

For any foam control program to be effective, it is imperative that all such additives be added at the minimum amount necessary to provide for good operation and product quality (5). In addition, Eisele and Hoffman (15) have developed a preparation which when used as paper size results in no foam formation either in the beater or the headbox. This preparation is basically a non-crystallizing reinforced rosin size with a high free rosin content. Preparation procedures are described in the referenced article.

Sulfate kraft pulping frequently results in cooking liquor/foam being pulled into the digester gas relief system. This is due primarily to alkali

FIGURE 8
BROWN STOCK WASHING SYSTEM AT SKOOKUMCHUCK (8)

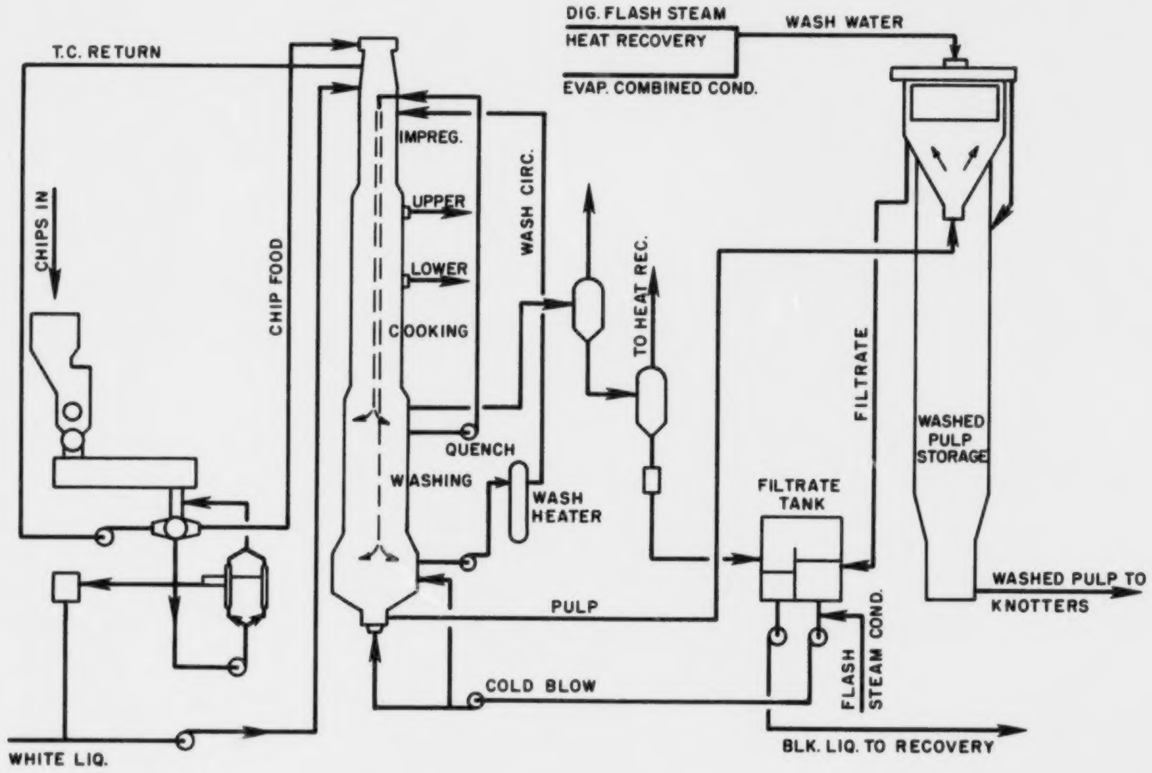

DIG. FLASH STEAM
HEAT RECOVERY
EVAP. COMBINED COND.
WASH WATER
T.C. RETURN
CHIPS IN
CHIP FOOD
IMPREG.
UPPER
LOWER
COOKING
QUENCH
WASHING
WASH CIRC.
WASH HEATER
TO HEAT REC.
FILTRATE
FILTRATE TANK
WASHED PULP STORAGE
WASHED PULP TO KNOTTERS
PULP
COLD BLOW
FLASH STEAM COND.
WHITE LIQ.
BLK. LIQ. TO RECOVERY

FIGURE 9

BROWN STOCK DIFFUSER EFFICIENCY VS. DROPLEG CONSISTENCY(8)

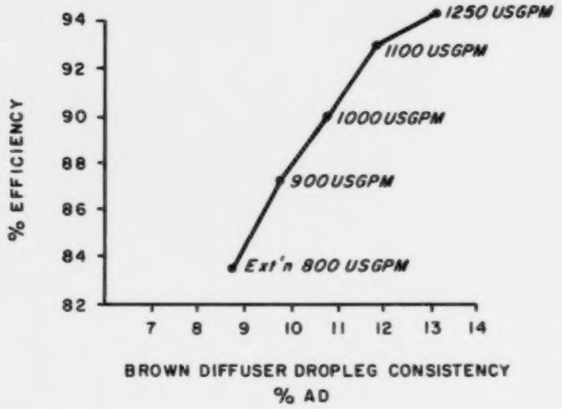
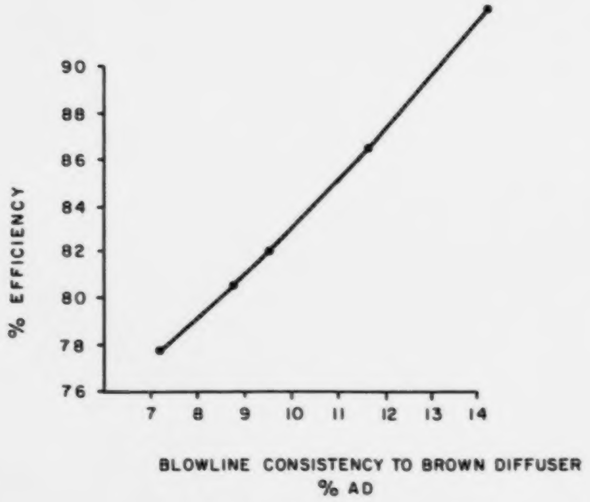


FIGURE 10

BROWN STOCK DIFFUSER EFFICIENCY VS. FEED CONSISTENCY(8)



reacting with resin to form soaps. These soaps then reduce the liquid surface tension and cause foam. Cowherd (16) reports of a device to automatically control the digester gas off system. This device is based on the difference in electrical conductivities of the vapor and liquid phases. An electrode is inserted in the gas off line to determine which is present - liquid or gas. When liquid is detected, steam blow back is instituted until the gas phase returns. This action is reported to insure the removal of gas rather than cooking liquor and foam.

Black liquor from brownstock washers is known to contain large quantities of tall oil soaps which promote foaming. Ellerbe (6) reported that removal and recovery of these soaps dramatically influences evaporator operation in that:

1. It increases the time between boilouts, and
2. It reduces the frequency of evaporator upsets

Both of these factors directly affect liquor losses and the attendant foaming and pollution problems (6, 11). In conjunction with this, Little (28) has developed a process whereby kraft black liquor can be recovered without using evaporators and boilers. The process, as described in the referenced report, is based on the use of fluidized bed techniques and is claimed to completely eliminate the foam problems encountered during the oxidation of black liquor.

Ellerbe also states that soap removal from the weak liquor storage tanks is just as important since most evaporator upsets will be traced to pulling soap into the feed during low liquor inventories. Subsequent foaming within the evaporators creates an unstable operation which is again usually corrected only by a boilout. It is interesting to note that much of the toxicity in evaporator condensates is attributed to foam carryover (11).

Foam quantities within pulp and paper mills may also be eliminated or at least significantly reduced by merely modifying liquid and stock handling procedures. Consider, for example, that foam is normally generated by aerating a liquid containing surfactants. If the liquid is not aerated, foam will not be generated. It then stands to reason that the elimination of free falls such as at weirs, at the drop leg of seal tanks and out of screens will help to reduce foaming. This was demonstrated by Schweizer (18) who found that reconstruction of a knot catcher reduced the free air content by 30 percent. There was a corresponding decrease in foam formation. According to Hercules (5) and Nuttall et.al. (17), other techniques which should also be effective are:

1. Tighten pump packing glands to prevent air from entering the unit,
2. Extend pipe lines to the bottom of vessels into which they discharge, and
3. Eliminate the use of larger capacity pumps than necessary.

Waldichuk (29) studied the foaming characteristics of effluents from three kraft pulp mills and concluded:

1. Caustic extraction - washer effluent is the primary cause of foam in kraft bleaching operations.

2. Voluminous amounts of stable foam are created when caustic effluent is mixed with chlorination and calcium hypochlorite stage washers effluent.
3. Zinc-hydrosulfite washer effluent decreases foam stability when added to the alkaline and/or acid waste streams prior to their mixing. This may, however, increase the initial volume of foam.
4. Green liquor dregs, when present in at least a 1 percent concentration, can reduce the volume of foam in a mixture of alkaline and acidic bleach effluents. However, dregs are not normally sewered with bleaching effluents.
5. Dilute solutions of black liquor readily foam when mixed with either alkaline or acid waste streams and introduced into coastal sea waters.

Ellerbe (9), in reporting on various solutions to foam problems, states that there are at least two items which do not normally receive the attention they deserve:

1. Control of the alkali residual at the end of the cook, and
2. Control of the first stage liquor solids concentration.

Ellerbe pointed out that pH has a known effect on foam stability in that the lower the pH the less stable the foam. He also noted that weak liquors may have stronger foaming tendencies than concentrated liquors. However, it is normal practice to discharge the weakest possible liquor. Control of each of these parameters should reduce foaming tendency.

Though not specifically referenced in the literature, there are several other internal modifications which may also be used to control foam. These include the following:

- Neutralization of waste acid from chlorine dioxide generating plants
- Separation of streams with differing pH values
- Controlling the use of $CaCO_3$ as a filler or coating pigment since CO_2 will be released under mildly acidic conditions and possibly contribute to foam generation.

Foam may also be a problem in paper mills. Berger (19) reports that in the manufacture of fine paper, foam is due primarily to:

1. The formation of CO_2 when alum is added
2. The use of dyes
3. Mechanical beating of air into the stock

Remedial actions suggested include the use of steam or water sprays or the addition of kerosene. Berkman (20) further states that foam occurs only in moving pulp when the water pH is above 7. He suggests using a water at pH 5-6, avoiding excess beating and decreasing the alum used for sizing to reduce foam problems.

Kress et al (21) report that calcium sulfite filled broke can also cause excessive foaming. They attribute this to the pressure of "colloidal calcium sulfate particles formed by partial oxidation of the calcium sulfite at pH values below 5." Remedial actions which they recommend include provisions for greater aeration to oxidize the sulfite to sulfate and greater detention time to allow the fine calcium sulfate particles to build up. Rawling (22), on the other hand, feels that the oxidation of sulfite to sulfate should be retarded to inhibit foaming. To accomplish this, he suggests adding a water soluble non-reducing acid salt such as sodium phosphate or a reducing agent such as sodium thiosulfate. It should be noted that both references 21 and 22 represent archaic methods that are no longer generally used.

Since air is a prime factor in foaming, stock deaeration would certainly help to prevent a foam problem. The modernized Deculator process is reported by MacGregor (23) to accomplish just this. The process uses a simple overflow system which is elevated to provide barometric removal of the headbox flow and recirculated overflow. This, in turn, eliminates modulating flow or level controls and provides for complete deaeration. Berlyn (24) reports on a similar device which he terms a hydrokinetic headbox to introduce paper stock to the machine without entraining air. Tischenko (25) also describes a foam preventing device. This device, however, is installed prior to the headbox and actually promotes foaming. The foam thus formed is then removed via a vacuum pump and the deaerated stock is directed to the headbox.

Hercules (5) has reported on foaming problems which occur when using Fourdrinier paper machines. These problems are believed caused by an increase in the number of air bubbles due to high surfactant concentrations. Four possible solutions were presented:

1. Lower the stock consistency to allow greater air release,
2. Slow the operating speed to extend the length of time the web remains fluid and thereby increase chances for air being released,
3. Increase the wire length to again extend the length of time the web remains fluid, or
4. Incorporate a deculator or other air disentrainment device.

Although alternates 1, 2 and 3 would reduce foam, they are generally not considered practical solutions because they would also reduce paper production.

Also recognizing the foaming problems with Fourdrinier machines, the Black-Clawson Co. (26) reports of a steam chamber which prevents the entrainment and trapping of air between the lower lip of the slice and the breast roll. The device is reported to remove air bubbles in the wire as well. Broughton (27) reports on another foaming problem which occurs within the vacuum control assembly standpipe. This problem, however, is solved by "directing a fresh water spray across the standpipe and into the conduit leading to the control valve used to regulate standpipe vacuum."

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APPENDIX C

BATTELLE LABORATORIES REPORT

REPORT

on

CHEMICAL CHARACTERIZATION OF RIVER FOAM

Jordan Company Contract #68-03-2605
Work Directive Number 2 - Phase 2

to

E.C. Jordan Co., Inc.

October 26, 1979

Prepared by

A. Bjorseth, R. Riggin, S. Lucas

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October 26, 1979

Bruce K. Wallin, Ph.D.
Edward C. Jordan Co., Inc.
P.O. Box 7050, Downtown Station
Portland, Maine 04112

Dear Bruce:

Please find enclosed our report entitled "Chemical Characterization of River Foam". The report describes our progress to date and is divided into two parts: a) GCMS studies of extractable resin acids and, b) characterization of non-extractable materials. As described in the report we still have certain items of work to be completed.

As of September 30, 1979, we have spent a total of $9,310 leaving a remaining balance of $13,930.

I apologize for the delay in getting this report to you.

Sincerely,

Alf Bjorseth

Alf Bjorseth
Associate Manager
Analytical and Environmental
Chemistry Section

AB/bsf

Enc.

cc: M. Strutz, EPA

50 Years Of Service
1929–1979

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CHARACTERIZATION OF NONEXTRACTABLE MATERIALS IN RIVER FOAM

Summary

The purpose of this portion of our study is to chemically characterize the materials, present in collapsed river foam, which are not extractable using methylene chloride at acid pH. A preliminary report of our findings was presented on 18 June 1979 as is attached as Appendix A. Considerable work has been conducted since then, as described in the experimental section of this report.

Our findings to date are summarized below:

1) Total organic carbon (TOC) in the extracted foam sample is ≈ 490ppm. However, if the sample is concentrated to dryness on a rotating evaporator at 50°C and reconstituted it contains only 60 ppm. - 350 before extraction
This implies that the majority of the TOC is volatile and could perhaps be residual solvent from the original extraction.

2) Total carbahydrate in the sample is estimated to be ≈ 48ppm, using the thymol/sulfuric acid test and < 10ppm using the anthrone test. Use of cellulase enzyme was not successful as it interfered with the assay.

3) Total phenolic concentration is estimated to be 15ppm using Folins reagent.

4) Total protein concentration is estimated to be ≈ 15ppm using the Kjehdahl nitrogen procedure.

5) Total methylene blue active substances (alkyl benzene sulfonates and sulfates) are estimated to be 46ppm.

6) Only ≈ 20ppm of the TOC present in the sample is extractable with isbutanol.

SUMMARY

Characterization of Extractable Materials in River Foam by GC/MS

Two samples of material extracted from river foam due to pulping mills have been methylated with diazomethane and analyzed by glass capillary gas chromatography/mass spectrometry. Analysis of the GC/MS data has shown:

1. The two samples are essentially identical.
2. The samples are composed of relatively few types of materals. Principally these are fatty acids, compounds related to the phenanthrene nucleus resin acids, and a wide range of materials which have been tentatively identified as phenolic compounds from lignin. ←
3. Specific analysis for the consent decree phenols shows that phenol, dimethyl phenol, and the chlorophenols are not present in the samples above the microgram level.
4. The sample consists of such a plethora of closely related, co-eluting materials that GC separation is not at all optimal. Some partitioning of these samples is suggested for future work. ← future work
5. Essentially all of the sample components have relatively high molecular weights, with 90% of the sample eluting from the glass capillary column between 160°C and 280°C with an unresolved "hump" of peaks at 240°C.

REPORT

on

CHEMICAL CHARACTERIZATION OF RIVER FOAM

Jordan Company Contract #68-03-2605
Work Directive Number 2 - Phase 2

to

E.C. Jordan Co., Inc.

October 26, 1979

INTRODUCTION

This report describes our progress to date on contract number 68-03-2605. The purpose of this study is to chemically characterize the components associated with pulp wood processing in the state of Maine.

This report is divided into two subsections; a) GCMS characterization of extractable materials and b) chemical characterization of non-extractable materials. Our studies to date have focused on collapsed river foam samples and is described in the subsections of this report.

GC/MS ANALYSIS OF THE EXTRACTABLE ORGANIC MATERIALS IN COLLAPSED RIVER FOAM BELOW PULPING MILLS

INTRODUCTION

The following work has been performed to provide data relevant to understanding the chemical parameters which operate to produce foaming of surface waters below wood pulping mills in the state of Maine. In this particular aspect of the work we have analyzed organic meterial which has been extracted with methylene chloride from an aqueous field sample of collapsed river foam. Two extract samples originating from foam collected on 1/29/79 (sample 1) and 3/5/79 (sample 2) were submitted for analysis by GC/MS. The object of the analysis was to identify or characterize as many separate compounds of the complex extract as possible. In addition, specific inspection of the GC/MS data for the presence of the eleven "consent decree" phenols has been performed.

EXPERIMENTAL

Storage, Handling and Residue Weights

Samples were received in sealed glass ampules. The samples were transfered to 2 ml screw cap (teflon lined) vials for further storage and handling. All sample storage was at -10°C. An aliquot of each sample was allowed to evaporate to dryness on a tared piece of aluminum foil, and the residue weight was determined using a Mettler model ME30 micro balance (readout to 1 μg).

Diazomethane Derivitization

An amount of sample sufficient to provide 5 mg and 3 mg (evaporated residue basis) of samples 1 and 2, respectively, was diluted to 500 μl for diazomethane derivitization with 10:1, diethyl ether: methanol (both Burdick and Jackson "DIG" grade and diethyl ether was from a freshly opened bottle specified as containing no preservatives). Phenol, D-5 4 μg, was added as an internal standard. Gaseous CH_2N_2 in a N_2 stream was bubbled through the sample until the change in color indicated the samples were saturated with CH_2N_2. After standing at room temperature for about 1 1/2 hours, the solvent volume was reduced under a very gentle N_2 flow to between 50 and 150 μl. Two internal standards were added: 4 μg anthracene, D-10 and 2 μg hexaethylbenzene.

GC-MS Analysis

A slightly modified Finnigan 3200 GC-MS system interfaced to a Systems Industries System/150 data system was used for sample analysis. The instrument was operated in the EI mode (70 eV) scanning 40 to 450 amu with an approximately 2.5 sec scan time. The column was a 30 meter X 0.22 mm glass capillary coated with OV-1. Chromatography parameters were: injector temp., 275°C; transfer line temp., 260°C; Helium carrier flow velocity, 26 cm/sec; temperature program: room temp. 3 min., 50°C 3 min., 50°C to 280°C at 4°C/min; 2 μl of sample was injected, splitless mode.

GC-MS Data Reduction

Mass spectra of discernable GC peaks and shoulders (with appropriate background subtraction) were matched using Finnigan INCOS software against the most recent NBS/NIH/EPA mass spectral data base (31,600 unique compounds). The data was specifically searched for the "consent decree" phenols as well as classes of compounds of interest using special Battelle-written software. All GC-MS data that was acquired has been stored on 9-track magnetic tape.

RESULTS AND DISCUSSIONS

Some General Aspects

The appearance and residue weights of the two samples were as follows:

- Sample 1 (1/29/79): tan-orange color, nearly clear, about 1 to 2 μl water (heterogeneous) 0.4 ml total volume. Residue weight: 5.4 mg total.
- Sample 2 (3/5/79): blood-red, clear, about 0.3 μl H_2O. Residue weight: 46.1 mg total.

Inspection of the two samples when received revealed that the 1/29/79 sample had leaked a very noticable amount of material through an improperly made seal at the top of the glass ampule. Thus, the 5.4 mg (total) of the 1/29/79 sample may represent an unknown fraction of the orginal foam extract.

Analysis of seven samples by GC-MS was performed. Of these seven, the following five samples were derivitized with diazomethane in simultaneous, parallel fashion as described under "Experimental".

1. A derivitization process blank, denoted "Blank"
2. A standard of "Consent Decree" phenols (Supelco commercial standard) 1.5 μ each , total, denoted "Phenol Standard"
3. Foam sample #1, 2.95 mg, residue weight basis, denoted "1/29/79 Foam"
4. Foam sample #2, 5.0 mg residue weight basis, denoted "3/5/79 Foam"
5. Foam sample #2 plus "Consent Decree" phenols, 4 μg each, denoted "3/5/79 Foam Spike".

In addition, the two foam extract samples were also analyzed by GC-MS as received, i.e., without diazomethane derivitization or dilution.

The complete set of reconstructed gas chromatograms (RGC's) for all GC-MS analyses are shown in Appendix 1. The GC-MS data for the underivitized "as received" analyses (Figures 2 and 3, Appendix 1) does not appear to yield any information which is significantly different from that of the diazomethane derivitized sample. Thus, no attempt has been made to interpret this data.

Deuterated Stearic Acid

Perdeuterated (D-35) stearic acid was added by the sponsor to the collapsed foam before extraction in the amount of 1 mg per liter. The purpose of this deuterated internal standard addition was to allow a quality control check of the GC-MS analysis as well as to provide the possibility for some rough quantitation of sample components on a per liter of collapsed foam basis. Unfortunately, the amount of stearic acid-D-35 added was somewhat high for this purpose since it was detected as one of the largest sample components, and many of the ions at lower mass were saturated. Nevertheless, it has been possible to roughly quantitate the amount of stearic acid-D-35 in the 3/5/79 sample using a response factor derived from a standard run containing hexaethylbenzene, HEB, (internal standard) and methyl stearate-D0:

$$\text{SA-D35 } (\mu\text{g}) = \text{aliquot factor} \times \text{ratio (MW)} \times \frac{\text{area (MS-D35)}}{\text{area (HEB)}}$$

$$\times \text{ Resp. Fact.} \times \text{HEB in Sample } (\mu\text{g})$$

where 1. SA-D35 = quantity of stearic acid D-35 in the sample Battelle received

2. aliquot factor = reciprocal of the fraction of the sample used for GC-MS analysis = 9.22

3. ratio (MW) = ratio of the molecular weights of the free acid to the methyl ester, 319/333 = .96

4. area (MS-D35)/area (HEB) = area of the ions in the molecular ion region of methyl stearate-D35 divided by the area for the molecular ion of the internal standard, hexaethylbenzene (taken from the sample analysis data), 52210/34755 = 1.50

5. Resp. Fact. = ratio of methyl stearate to HEB (μg) in standard run times ratio of (area of the m/e 246 (HEB)) to (area methyl stearate in molecular ion region) = 10.43.

Using the above data, we calculate that there was 280 ± 50 μg of stearic acid-D35 in the sample, as received. The above quantitation essentially amounts to the use of a one point (plus the origin) standard curve; thus, the somewhat large error limit (20%) is not unexpected. Comparison of this value with the theoretical one (based on: 1. the number of liters of collapsed foam from which the 3/5/79 sample was produced, 2. the 1 mg/l spiking level, and 3. the fraction of sample sent to Battelle for GC-MS analysis) will provide a estimate of the derivitization effectiveness and acceptability of the GC-MS data for quantitative approximation. However, due to the somewhat excessive amount of stearic acid-D35 present, such judgements should be deemed tentative.

"Consent Decree" Phenols

Figure 2 of Appendix 1 shows the RGC of the 1.5 ug "Consent Decree" phenol standard (15 ng, each, injected splitless) and Figure 5 of Appendix 1 shows the HGC of the 3/5/79 sample spiked with the "Consent Decree" phenols (4 ug each). Peaks corresponding to the free phenols and/or their methyl ethers are labeled in these two chromatograms. The poor detection performance toward the nitro phenols is not surprising. It is due to activity of metal components in the mass spectrometer transfer line. The same capillary column used for these GC-MS analyses showed excellent performance for the nitro phenols when checked in an FID gas chromatograph. Certainly, the most important components with regard to pulp mill effluents are phenol and the chlorophenols for which Figures 2 and 5, Appendix 1, show excellent performance.

As explained under "Experimental", each derivatized sample was spiked with 4 ug of phenol-D5 deuterated internal standard before processing. The purpose of the phenol-D5 was two-fold:

1. To monitor the effectiveness of the diazomethane deritivatization
2. Allow for the quantitation of the "Consent Decree" phenols which might be present.

The extent of phenol derivatization was determined from the GC peak area ratios in the 1/29/79 and 3/5/79 samples. It was found to be 19% in the former case and 40% in the latter. This range of variability is usually encountered for phenol. The chlorinated phenols always derivatize completely. Mass spectra of phenol-D5 and phenol-D5 methyl ether from the 1/29/79 and

3/5/79 samples, respectively, are shown in Figures 1 and 2, respectively. On the basis of these two figures, we can say definitively that phenol is below the detection limit in the 1/29/79 sample (less than 75 ng phenol in the total sample, as received) and present in the 3/5/79 sample at about 700 ± 100 ng.

The GC-MS data of the 1/29/79 and 3/5/79 derivatized samples have also been specifically searched for the presence of the phenols for which the "Phenol Standard" data analysis, Figure 2, Appendix 1, indicates good detection capability. The software employed for this specific search was developed at Battelle and provides for extremely sensitive detection of very low level sample components in an automated fashion. Table 1 lists the detection and quantitation results for these two GC-MS sample analyses. Quantitation is based on a response factor derived from the "Phenol Standard" run described above (Figure 2, Appendix 2) in an analogous fashion to the response factor method used to quantitate the stearic acid-D35, above.

TABLE 1. Results of Specific Search for "Consent Decree" Phenols

Compound	Sample	Amount in Total Sample Received (ng)
Pentachlorophenol	1/29/79	31
	3/5/79	160
2,4,6-trichlorophenol	1/29/79	11
Phenol	1/29/79	< 75
	3/5/79	700

The values shown in Table 1 for the chlorophenols are extremely low, and should be interpreted only as an indication that a trace of each compound shown is present. Use of the response factor method in the cases of pentachloro and trichloro phenol involves an extrapolation to nearly two orders of magnitude lower concentrations than those of the internal standard and the respective phenols from which the response factors were derived.

Identification Results

General Features

In Figures 1 and 2 are shown reconstructed gas chromatograms (RGCs) for GC-MS analysis of the 1/29/79 and 3/5/79 foam samples, respectively. There are four key observations to note regarding Figures 3 and 4:

(1) The samples consist almost entirely of relatively high molecular weight material.

(2) While there are six to ten components which are somewhat prominent in the chromatograms, probably 80-90% of the sample consists of a multitude of small amounts of closely related--and poorly separated--components, i.e., the late eluting "hump".

(3) Most of the identifiable components are fatty acids (saturated and unsaturated) and materials which are related to the family of natural products of wood which are based on the phenanthrene nucleus (resin acids and related compounds and biodegradation products).

(4) The 1/29/79 and 3/5/79 samples are strikingly similar.

Detailed Interpretation

The GC-MS data for the 1/29/79 sample has received a relatively exhaustive effort to interpret the mass spectra of the GC resolved compounds. Interpretation of the GC-MS data of the 3/5/79 sample, however, has been done in less detail for the following reasons:

(1) The 1/29/79 and 3/5/79 samples are essentially identical. While this is clearly indicated by Figures 3 and 4, it is even more obvious from the selected ion chromatograms which appear in the next section of this discussion, "Characterization by Selected Ion Chromatograms".

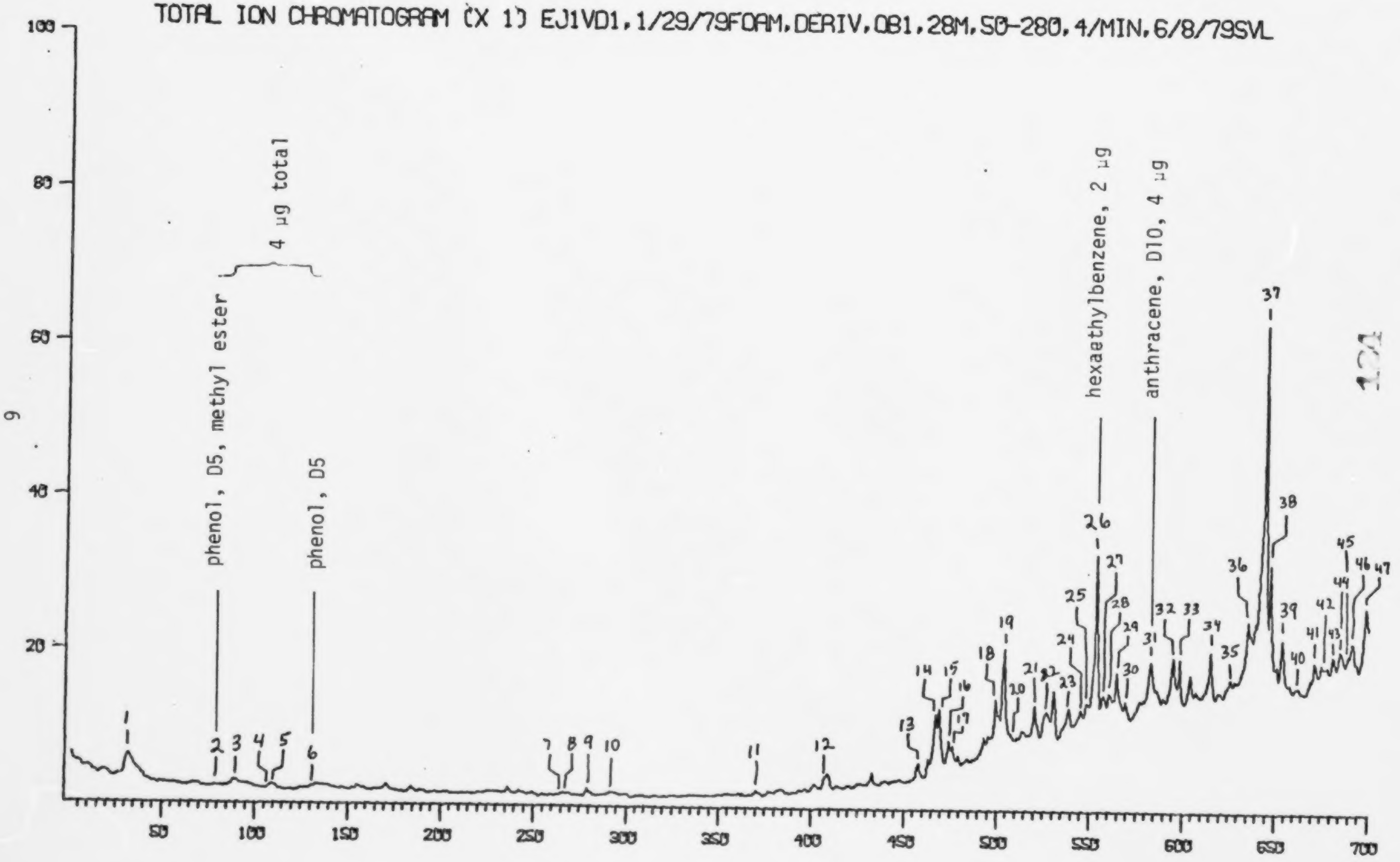
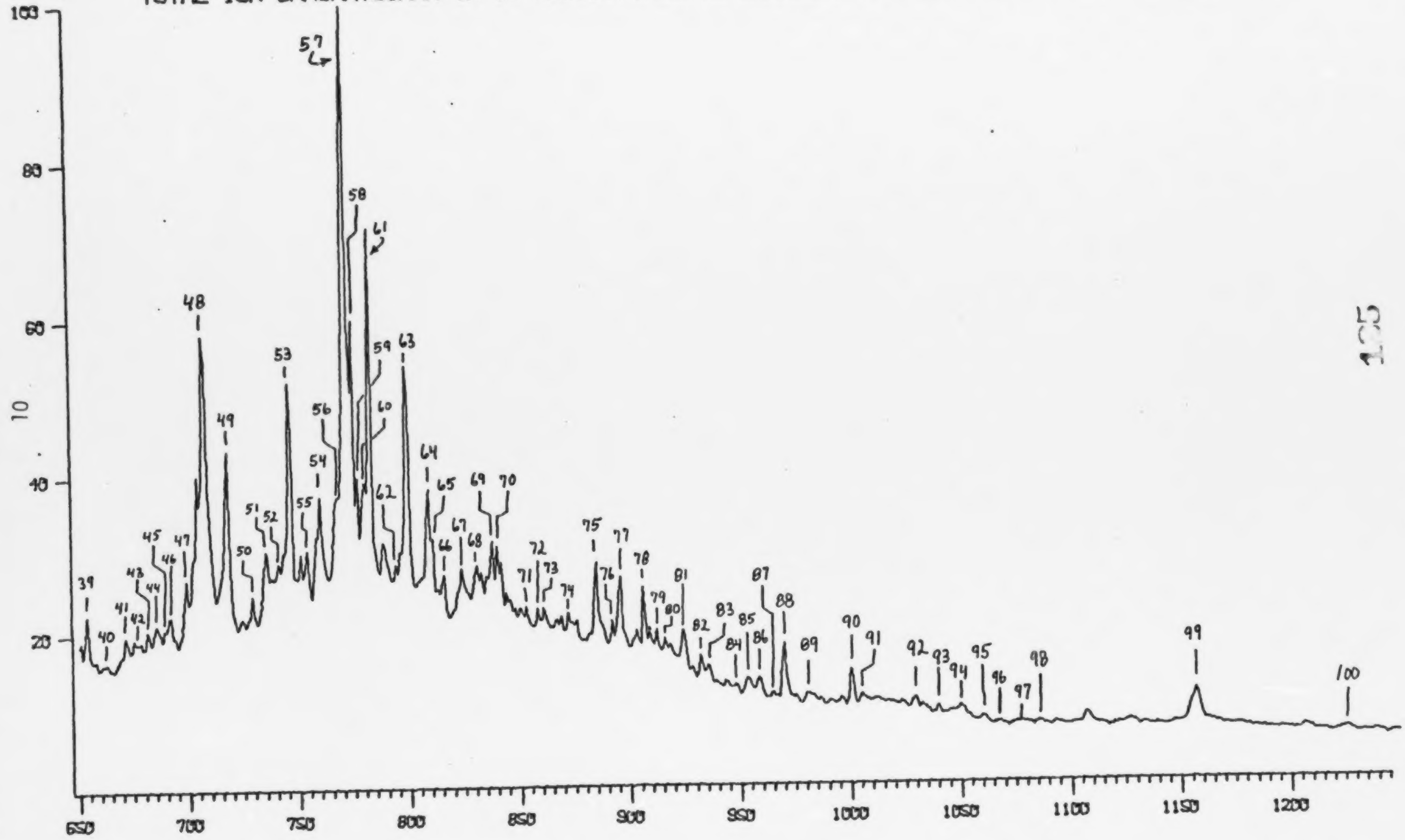


FIGURE 1. 1/29/79 SAMPLE, DIAZOMETHANE DERIVATIZED;
PEAK NUMBERS CORRELATE WITH TABLE 2



TOTAL ION CHROMATOGRAM (X 1) EJ1VD1,1/29/79FOAM,DERIV,OB1,28M,50-280,4/MIN,6/8/79SVL

FIGURE 1. CONTINUED

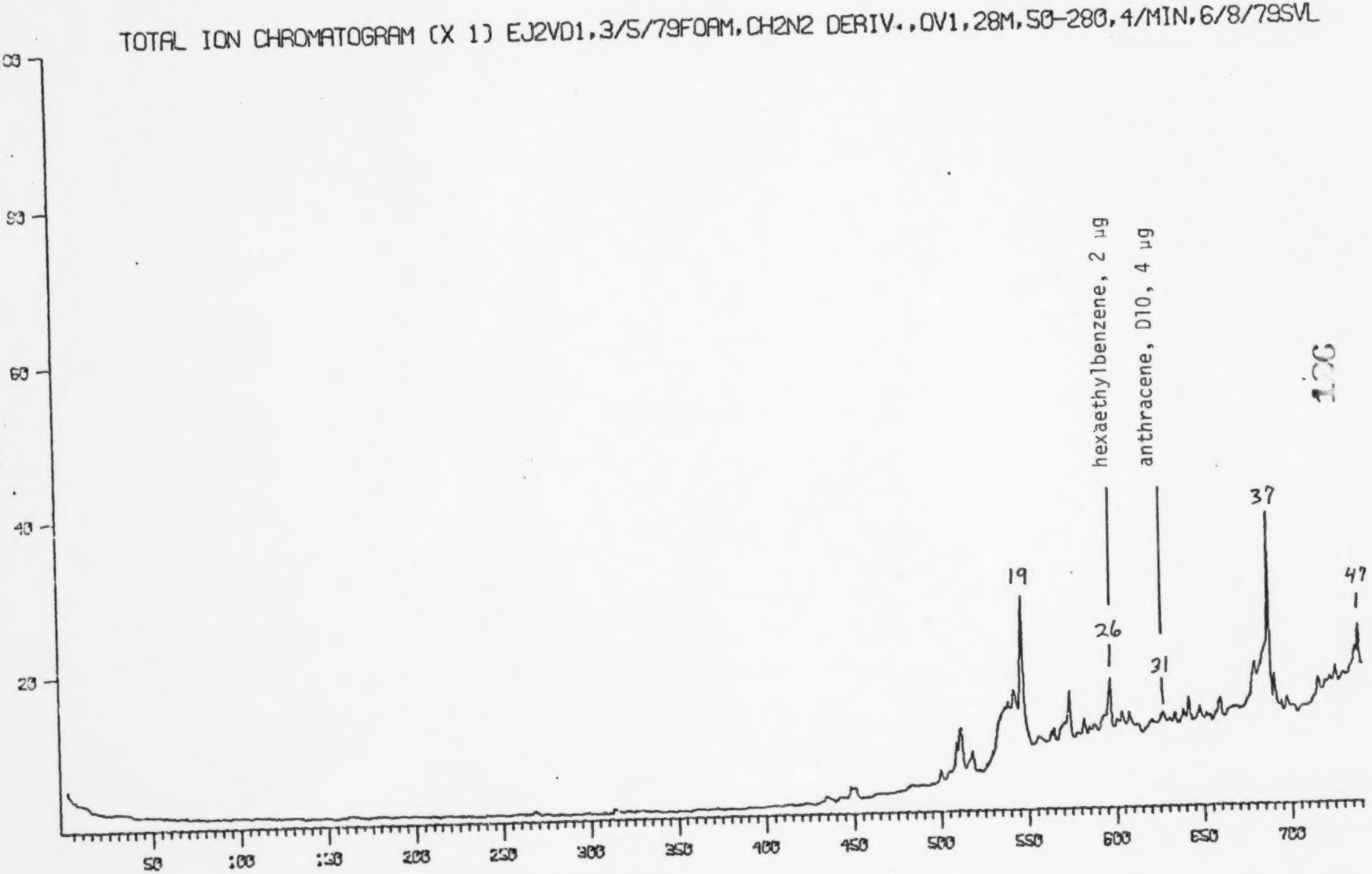


FIGURE 2. 3/5/79 SAMPLE, DIAZOMETHANE DERIVATIZED;
PEAK NUMBERS CORRELATE WITH TABLE 2

TOTAL ION CHROMATOGRAM (X 1) EJ2VD1,3/5/79FOAM,CH2N2 DERIV.,OV1,28M,50-280,4/MIN,6/8/79SVL

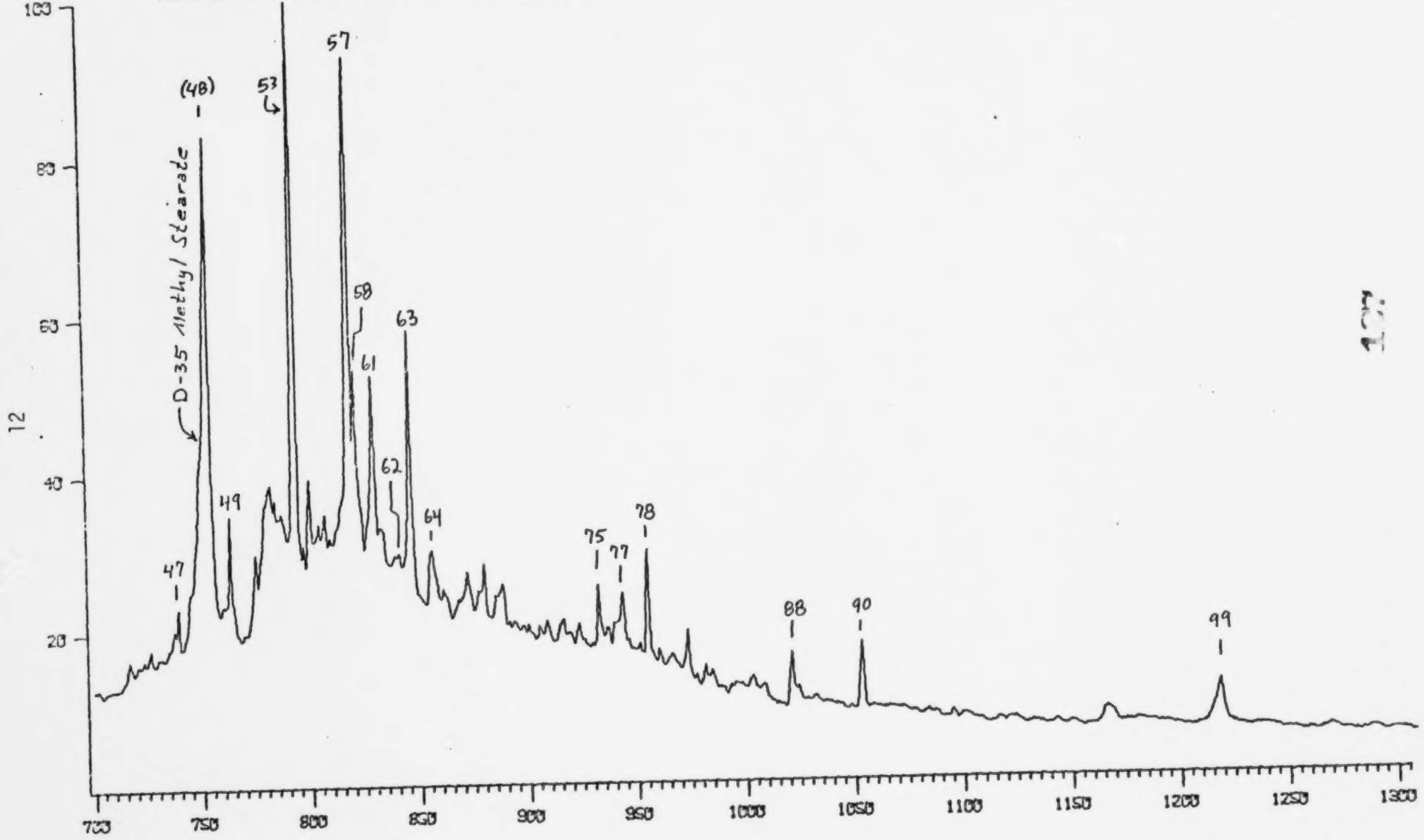


FIGURE 2. CONTINUED

(2) The 3/5/79 sample aliquot which was derivatized contained nearly twice the amount of material (residue weight basis) as the 1/29/79 sample aliquot. Because of this, there are more saturated ion current signals and GC peaks which overload the chromatographic capacity in the 3/5/79 sample data than in the 1/29/79 data. These two factors combine to make the GC-MS data for the former sample less interpretable than that of the latter.

Table 2 correlates the identification results of the 1/29/79 sample with the chromatogram of Figure 1. Some of the GC peaks which have been identified in the 3/5/79 sample and which correspond to identifications in the 1/29/79 sample are indicated in Figure 2 with the corresponding GC peak number used in Figure 1.

Of the 100 GC peaks in the 1/29/79 data (Table 2) which have interpretable mass spectra, 4 are internal standards, 4 are attributable as artifacts (siloxane compounds), 30 are strictly unidentifiable at the present time, and 62 have either been tentatively identified as a specific compound or are confidently identified as a member of a class of components (for example, as unsaturated fatty acid methyl ester, or phenanthrene nucleus-resin acid related, etc.). With the exceptions of a few phthalates, 2,4-D, and lithocholic acid, none of the identifications in Table 2 can be considered an unexpected component of pulping mill effluent. Unfortunately, the bulk of the sample constituents are not well separated on the GC column so that mass spectral interference results in less than optimal computer library matching and very difficult manual interpretation of the mass spectra. The largest GC peak in the chromatogram of Figure 1 (#45) is a resin acid related compound (the best computer match is for an isomer of abietic acid). Four of the largest 7 GC peaks are resin acid related compounds, while the other 3 are all fatty acids (detected as their methyl esters). These two classes of compounds account for 44 and 17, respectively, of the identified compounds while fatty substituted phenols account for 7 of the identifications and perhaps half of the unidentified listings in Table 2. The phenol class of compounds (related to lignin and associated breakdown products) is discussed in the next section.

Table 2. GC/MS Identification Results for the 1/29/79 Extracted Foam Sample

GC Peak No.	Spectrum minus Background	Retention Time	Relative Retention Time	Compound Name/Identification Information
1	31-28	7. 268	0. 182	A silicone, artifact?
2	79-73	10. 543	0. 264	Phenol-D5,ME
3	89-83	11. 202	0. 280	Hexanoic acid, ME
4	106-103	12. 310	0. 308	Weak, alkyl benzene?
5	109-104	12. 500	0. 312	Alkyl benzene
6	133-120	14. 013	0. 350	Phenol-D5
7	264-260	21. 917	0. 548	A silicone, artifact?
8	266-269	22. 037	0. 551	Cyclo siloxane, artifact?
9	279-276	22. 798	0. 570	Fatty alcohol
10	290-287	23. 442	0. 586	Capric acid, ME
11	370-367	28. 097	0. 702	Butyl butanoate, isomer
12	407-405	30. 290	0. 757	1,6-Dimethyl-4-isopropyl decalin
13	458-455	33. 357	0. 834	A C-6 substituted decalin
14	467-464	33. 903	0. 848	Alkyl tetralin + lauric acid, ME
15	469-471	34. 027	0. 851	Isomer of #12
16	474-472	34. 338	0. 858	A silicone, artifact?, + ?
17	479-481	34. 643	0. 866	An octahydro-C5-naphthalene
18	499-497	35. 873	0. 897	? MW 222, large m/e 121
19	505-501	36. 250	0. 906	4-Isoctyl phenol
20	509-503	36. 503	0. 913	2,4-D,ME (herbicide), weak, mixture
21	520-517	37. 193	0. 930	A reduced C-5 naphthol, MW 222
22	527-523	37. 632	0. 941	Isomer of #21
23	539-540	38. 387	0. 960	1,5-Dimethyl-4-isopropylnaphthalene
24	545-542	38. 763	0. 969	Mixture; inc. nonyl phenol?
25	548-547	38. 955	0. 974	Monobutyl phthalate, ME
26	553-550	39. 278	1. 000	Hexaethylbenzene, internal standard
27	557-555	39. 538	1. 006	An alkyl phenol
28	561-565	39. 798	1. 013	An alkyl phenol
29	564-562	39. 992	1. 018	Myristic acid, ME
30	569-572	40. 312	1. 026	Base peak 189, possible phenol
31	582-579	41. 145	1. 047	Anthracene, D-10, internal standard
32	595-592	41. 987	1. 068	2,5-Dimethyl-8-isopropylnaphthalene-1-ol
33	598-600	42. 182	1. 073	Trimethylmethano hexahydroazulene carboxylic acid, ME
34	615-617	43. 292	1. 100	Base peak 179, dialkyl dihydroxy benzene
35	625-623	43. 953	1. 117	Dimethylisopropylnaphthalene or azulene, MW 198
36	635-631	44. 627	1. 134	Mixture, inc. phthalate
37	644-640	45. 228	1. 149	Palmitic acid, ME
38	647-650	45. 427	1. 154	Dibutyl phthalate
39	654-656	45. 897	1. 165	? Good spectrum, base peak 165, MW 240

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Table 2. Continued

GC Peak No.	Spectrum minus Background	Retention Time	Relative Retention Time	Compound Name/Identification Information
40	662-664	46.433	1.179	Similar to #39, but MW 242
41	671-669	47.038	1.194	Mixture, inc. fatty acid, ME
42	675-673	47.307	1.201	Mixture, large m/e 113 + a phenanthrene cpd.
43	681-679	47.713	1.211	Margaric acid, ME
44	685-683	47.988	1.218	Resin acid related; MW 270
45	689-688	48.262	1.225	Match for a C-5 phenanthrene carboxaldehyde, MW 284
46	691-689	48.397	1.228	1,1,4a-Trimethyl-7-isopropyloctahydrophenanthrene, MW 270
47	699-696	48.943	1.242	MW 270 + large 107
48	707-712	49.492	1.255	Oleic acid
49	718-714	50.245	1.274	Stearic acid
50	729-726	51.010	1.293	((Isopropylphenyl)ethyl)dimethylcyclohexane carboxylic acid, ME, "opened" abietic acid
51	737-734	51.570	1.307	Match for dimethylisopropylphenanthrene carboxaldehyde (octahydro)
52	742-740	51.925	1.316	Similar to #51, but hexahydro?, MW=#51 + 2 = 280
53	746-742	52.207	1.323	Same match as #51, MW 278
54	760-763	53.202	1.348	Mixture, tris(chlorophenyl)phosphate + tetramethoxypropenyl benzene
55	754-752	52.772	1.337	1,4a-Dimethyl-6-methylene-5(3-methylpenta-2,4-diene decalin carboxylic acid, ME, MW 316
56	767-764	53.707	1.361	Similar to #54
57	772-764	54.065	1.370	Same match as #55 which is abietic acid related
58	775-769	54.277	1.375	5-(trimethyl-2-methylene decalin)-2-pentenoic acid, ME
59	777-778	54.418	1.378	Butyl benzyl phthalate
60	779-780	54.563	1.382	Similar to #61
61	782-780	54.778	1.387	MW 326, similar to resin acid, but add one CH2 + arachidic acid, ME
62	794-791	55.647	1.409	Abietic acid
63	799-803	56.007	1.418	?, Hydrocarbon-like
64	809-806	56.730	1.436	Base peak 185, match for phenanthrene carboxaldehyde
65	811-807	56.875	1.440	Match for a podocarpic acid, ME
66	816-818	57.238	1.449	Same as #65
67	823-821	57.750	1.462	A phenanthrene nucleus: resin acid related
68	828-826	58.117	1.471	Base peak 199, m/e 185, 295, 309; MW 324
69	838-835	58.855	1.489	Same match as #65
70	840-837	59.002	1.493	Behenic (C-22) acid, ME, + phthalate (octyl or cyclohexyl)
71	853-855	59.962	1.517	Match for abietic acid, ME
72	858-856	60.333	1.526	Lignin-related phenol?
73	861-864	60.557	1.532	Similar to #72
74	872-870	61.377	1.552	Siloxane, artifact?
75	885-879	62.348	1.577	Base peak 45, m/e 89, 135, 161, 311
76	892-890	62.872	1.590	Hydrocarbon-like with large m/e 171
77	896-899	63.173	1.597	Lignocenic (C-24) acid, ME
78	906-904	63.923	1.616	Base peak 117, m/e 135, 161, 339; MW 396? lignin related?

Table 2. (Continued)

GC Peak No.	Spectrum minus Background	Retention Time	Relative Retention Time	Compound Name/Identification Information
79	912-914	64.378	1.627	Siloxane, artifact?
80	916-914	64.680	1.635	Similar to #78
81	924-921	65.283	1.650	Good match for carotene
82	932-930	65.888	1.665	Similar to #78
83	935-938	66.115	1.671	Similar to #78
84	948-950	67.090	1.695	Similar to #78
85	954-950	67.542	1.707	Base peak 45, m/e 89, 117, 133, 161, 355; lignin related?
86	958-962	67.842	1.714	C-26 fatty acid, ME + siloxane
87	964-961	68.292	1.725	MW 360; fair match for trimethoxytrihydroxy flavone
88	970-967	68.740	1.737	Similar to #85
89	980-978	69.478	1.755	Similar to #85
90	1000-998	70.953	1.792	Base peak 117, m/e 135, 161, 383; lignin related?
91	1005-1003	71.323	1.801	Similar to #85
92	1029-1026	73.093	1.845	Similar to #90
93	1040-1037	73.893	1.865	Similar to #90
94	1050-1056	74.615	1.883	Lithocholic acid, ME; (3-hydroxycholonoic acid, ME)
95	1060-1057	75.337	1.901	Similar to #90
96	1067-1071	75.837	1.914	Similar to #90
97	1076-1072	76.477	1.930	Similar to #90
98	1086-1083	77.190	1.948	Similar to #90
99	1157-1150	82.230	2.092	Similar to #90
100	1225-1219	86.992	2.211	Similar to #90

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Characterization by Selected Ion Chromatograms

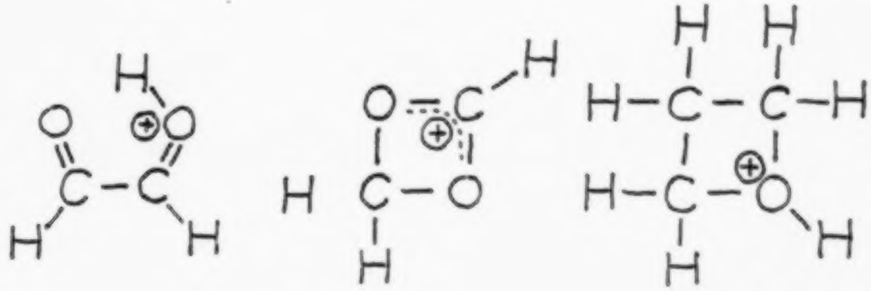
The problem of mass spectral interference due to the chromatographic overlapping of sample components was pointed out in the preceeding discussion. The result of this spectral interference is that the computer library matching results of these mass spectra are not optimal. Furthermore, many of the multitude of compounds which are related to the resin acids or their break-down products do not have their mass spectra entered into the computer data base so that correct computer identification results cannot be expected. Moreover, mass spectra of these compounds are extremely complex, and manual interpretation to the point of correct molecular structure identification is often impossible and nearly always not cost effective. For this reason, extracted ion current profiles have been utilized to obtain information about the types of molecular species present. A preliminary examination of the computer spectral matching results indicated that most of the compounds present could be classified into three categories:

1. Saturated and unsaturated fatty acids (detected as the diazomethane derivatized methyl esters)
2. Alkylated phenols (detected as the free acids).
3. Components related to the resin acids and their break-down products.

Fatty Acids

Detection of α,β-unsubstituted saturated fatty acids (as the methyl esters) using extracted ion current profiles of m/z 74 and 87 is highly sensitive and specific. These ions are also quite selective but less sensitive for α,β-unsubstituted mono- and di-unsaturated methyl esters of fatty acids. Methyl esters of fatty acids with greater degrees of unsaturation yield mass spectra nearly identical to those of olefins, and the m/z 74 and 87 detection may not be satisfactory--especially in the case of esters of conjugated polyunsaturated acids. Figures 3 and 4 show sets of selected ion chromatograms which clearly indicate the fatty acids (as the methyl esters) present in the 1/29/79 and 3/5/79 samples, respectively. The m/z 74, 87 trace indicated with 50% threshold is somewhat more selective since the intensity ratio, 74/87, must range between 0.5 and 2 in a spectrum or no extracted ion response will be recorded. The expected sequence of methyl esters of even carbon number (C-12 through C-24) fatty acids is clearly seen in Figures 5 and 6. Palmitic and stearic acids appear to comprise about 65 to 75% of the total saturated fatty acids which were present in the sample, with palmitic only slightly more concentrated than stearic. Evidence for relatively small concentrations of the odd carbon number fatty acids at C-15, 17, 19, 21 and 23 is also present in Figures 3 and 4. It should be noted that the selected ion (m/z 74 plus m/z 87) peak shown for oleic acid (methyl ester) in Fiqure 3 is relatively small compared to those of palmitic and stearic. However, this result is exactly reversed in the total ion chromatogram, and, indeed, the amount of oleic acid in the sample is probably about twice that of stearic acid. This is simply a result of a large amount of the ionization of oleic acid having occured at the double bond so that relatively less m/z 74 and 87 are formed. This observation is obscured in Figure 4 by the coelution of the very large methyl stearate-D35 and oleic acid.

Also shown in Figures 3 and 4 are single ion chromatograms for the methyl carboxyl ion, m/z 59, $(OCOCH_3)^+$, which is almost always present in the mass spectra of carboxylic methyl esters. Other ions with m/z of 59 which could interfere with its use for visualizing carboxylic methyl esters are $(CH_2OC_2H_5)^+$ from alkyl ethyl ethers, $(CH_3(COH)CH_3)^+$ from α,α-dimethyl alcohols, and the rearrangement ions:



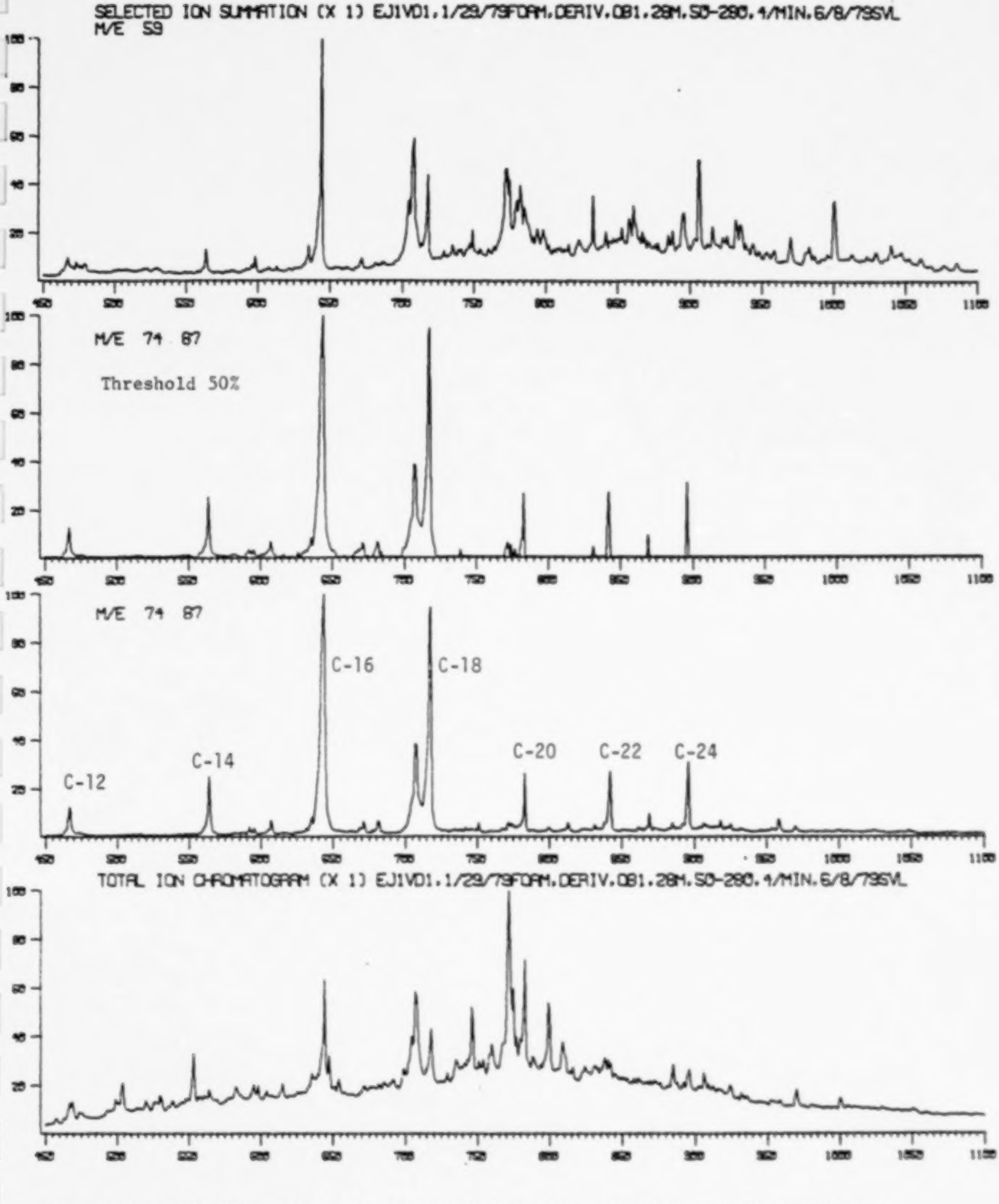


Figure 3. 1/29/79 Sample; Fatty Acid Methyl Ester Specific Ion Chromatograms

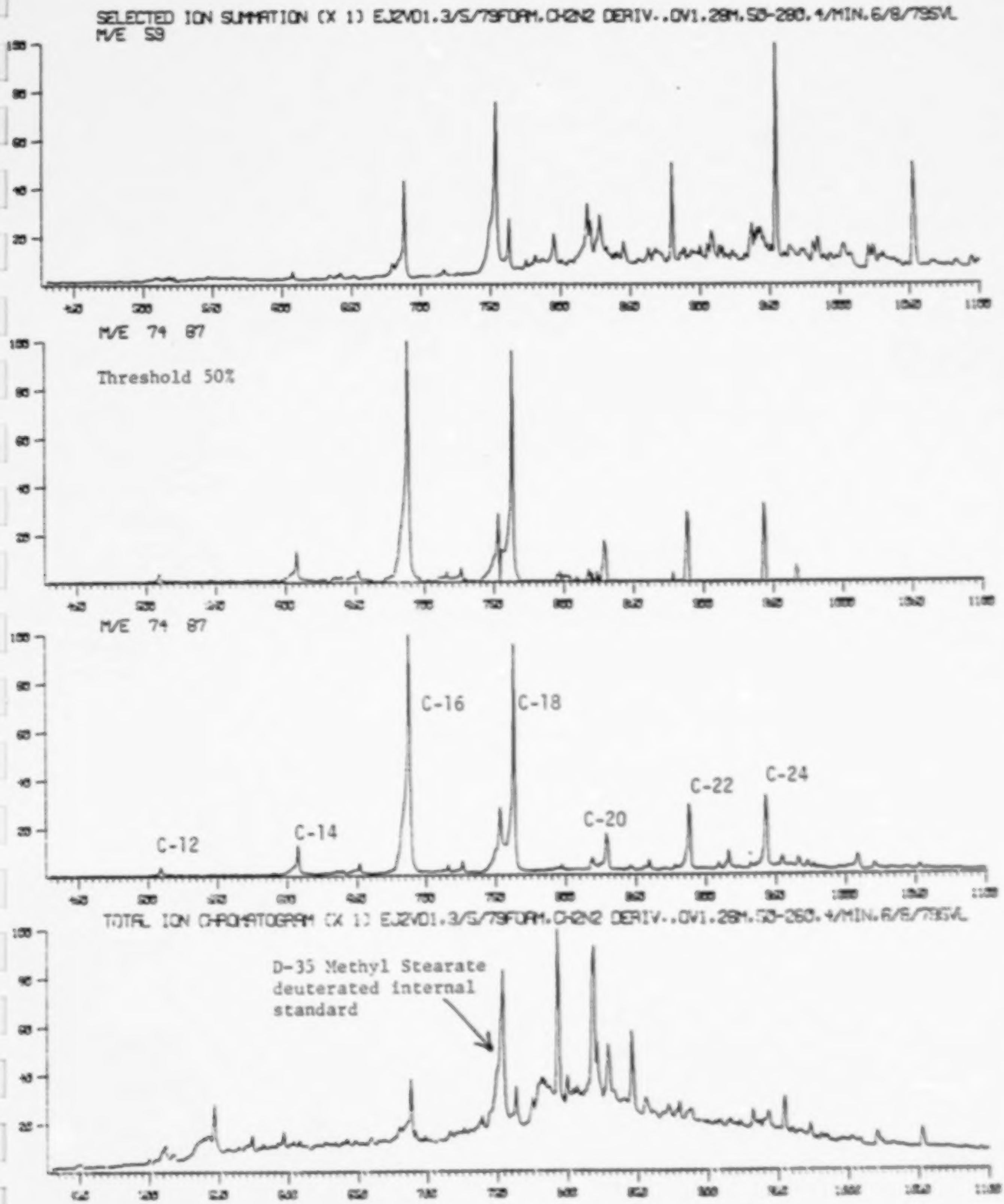


Figure 4. 3/5/79 Sample; Fatty Acid Methyl Ester Specific Ion Chromatograms

Considering the source of the present samples, the methyl carboxyl cation is the most likely m/z 59 possibility. Thus, one can interpret the m/z 59 traces in Figures 3 and 4 as indicating that most of the later eluting sample components contain one or more methylated carboxylic acid groups.

Alkylated Phenols. Detection of a number of alkylated phenols in the early phase of the elution profile "hump" (see figures 1 and 2 and Table 2) suggested that other species with alkylated phenol functionality might also be present. Figures 5 and 6 show selected ion chromatograms of the 1/29/79 and 3/5/79 samples, respectively, for ions which are indicative for some of the earlier eluting phenols. The m/z 107, 121 and 135 ions correspond to the formula $[OH(C_6H_4)(CH_2)_n]^+$ where n is 1,2 and 3, respectively. It was found that a number of late eluting components showed the m/z 107, 121 and 135 ions in similar abundance ratios to the earlier eluting alkyl phenols but also had a large m/z 117 ion which was often the base peak. The upper traces of Figures 5 and 6 show the enhanced response of the later eluting peaks when m/z 117 is added to the three phenol indicating ions. GC peaks which have m/z 117 as a major ion are indicated in the figure. Although successful identification of this family of compounds has not yet been achieved, a good possibility is that the phenols have their origin from lignin and various breakdown products.

Resin Acid Related Compounds. What compounds should be included in the category, resin acid related, is not entirely clear. In the present case, any compound which has a structure whose nucleus is the same as or a subset of that of abietic acid has been so classified. Included, of course, are all compounds with a phenanthrene nucleus. In addition, however, those compounds with a naphthalene nucleus (including decalins, tetralins and other partially reduced substituted naphthalenes) as well as "unfolded" phenanthrene backbones have been so classified. More often than not, for this plethora of compounds, there will not be a good computer spectral

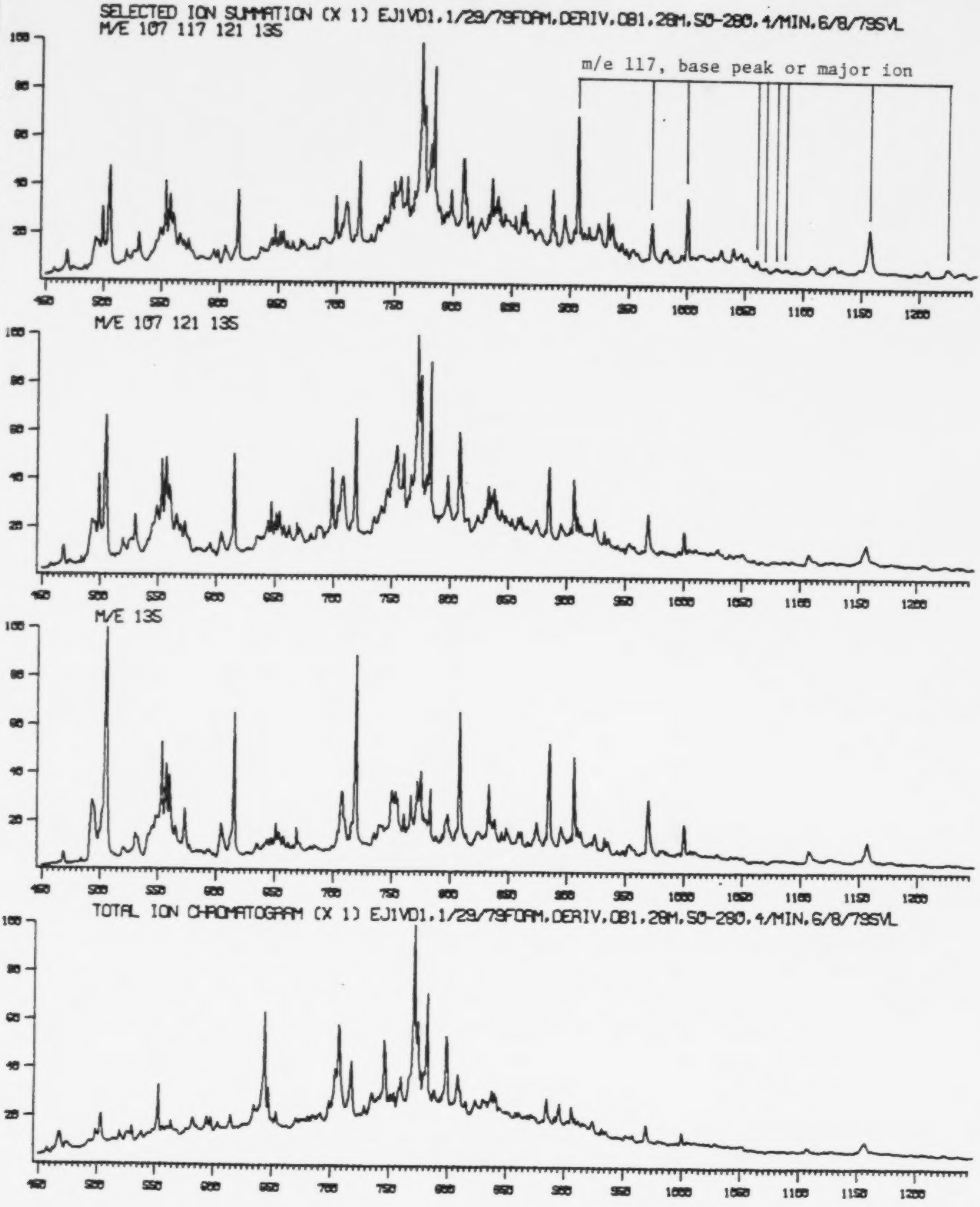


Figure 5. 1/29/79 Sample; Alkylated Phenol Indicator Ions, Specific Ion Chromatograms

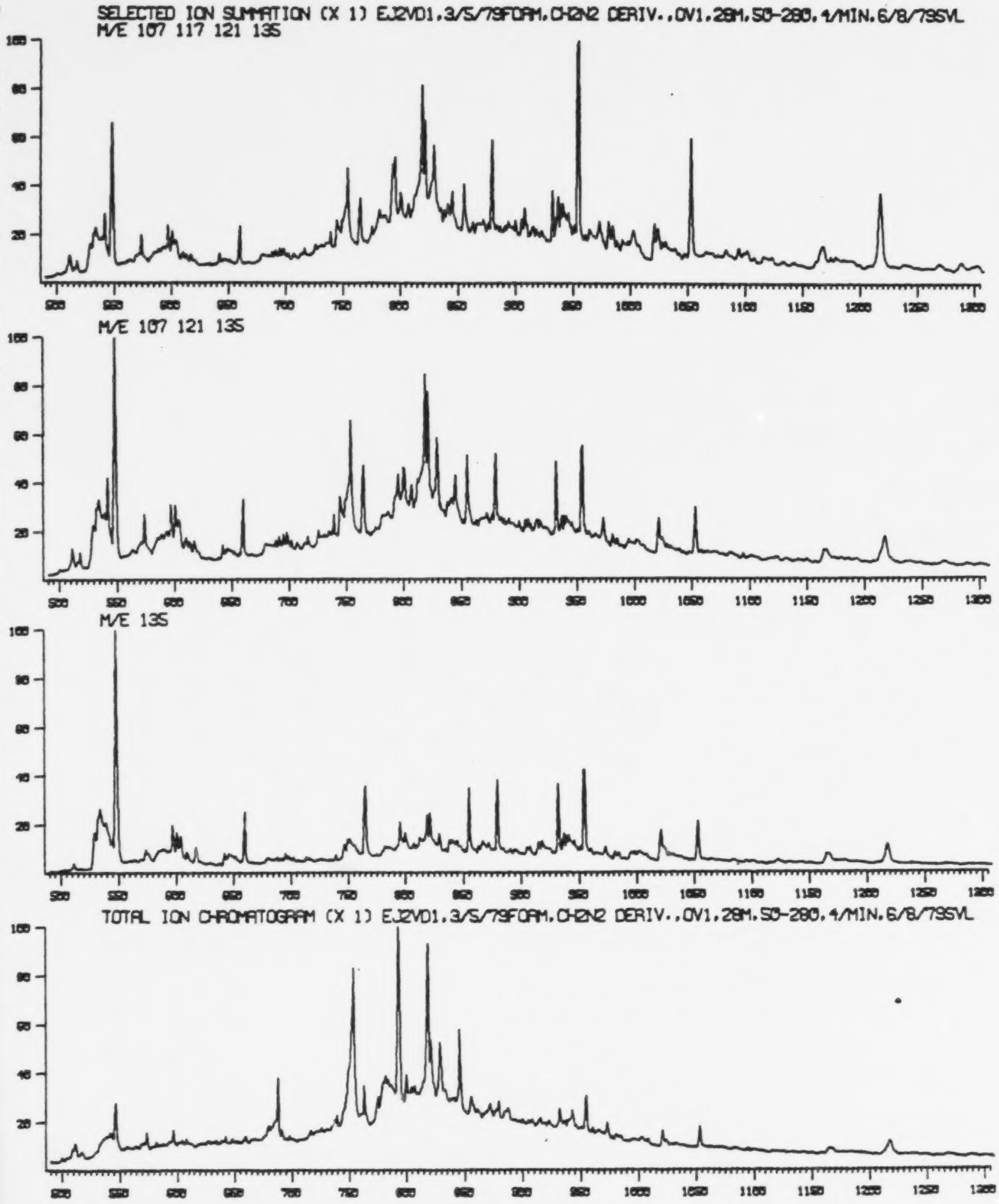


Figure 6. 3/5/79 Sample; Alkylated Phenol Indicator Ions, Specific Ion Chromatograms

matching hit. Instead, a few key similarities between the unknown mass spectrum and those of some resin acid related compounds which are in the spectral library data base will result in a number of poor to fair quality match "hits" for those compounds. Of course, this broad range of compounds does not have such unique indicator ions as was the case for the fatty acid methyl esters. Comparison of reference spectra of abietic acid (methyl ester) and a number of related compounds (including the naphthalene nucleus compounds) suggested that the ions with m/z 241, 255, and 256 were common and somewhat unique to many phenanthrene and naphthalene compounds while the ions with m/z 185 and 199 were somewhat less selective but more consistently found in the resin acid related compounds. Figures 7 and 8 show selected ion chromatograms using these two sets of ions for the 1/29/79 and 3/5/79 samples, respectively. The m/z 241, 255 and 256 ions show higher and lower molecular weight clusters (320 and 270, respectively) with the higher cluster tending to have more methyl esters. The m/z 185, 199 chromatograms show that many later eluting components are indeed due to resin acid related components. Figures 9 and 10 (1/29/79 and 3/5/79 samples, respectively) show selected ion chromatogram traces for three molecular weights of relatively common resin acid related materials: m/z 284, 1,4a-dimethyl-7-isopropyl-1,2,3,4,4a,9,10,10a-octahydro-phenanthrene-1-carboxaldehyde; m/z 314, dehydroabeitic acid, methyl ester; and m/z 315, abeitic acid, methyl ester. An additional trace at m/z 326 locates unidentified components which have a fragmentation pattern which is characteristic of a number of resin acid species. Somewhat surprisingly the methyl esters of abietic acid and dehydro-abeitic acid are not major constituents of these samples. Indeed, dehydroabeitic acid methyl ester is such a minor component that no distinct peak for it can be seen in the total ion chromatogram, and the specific ion search was required to find it.

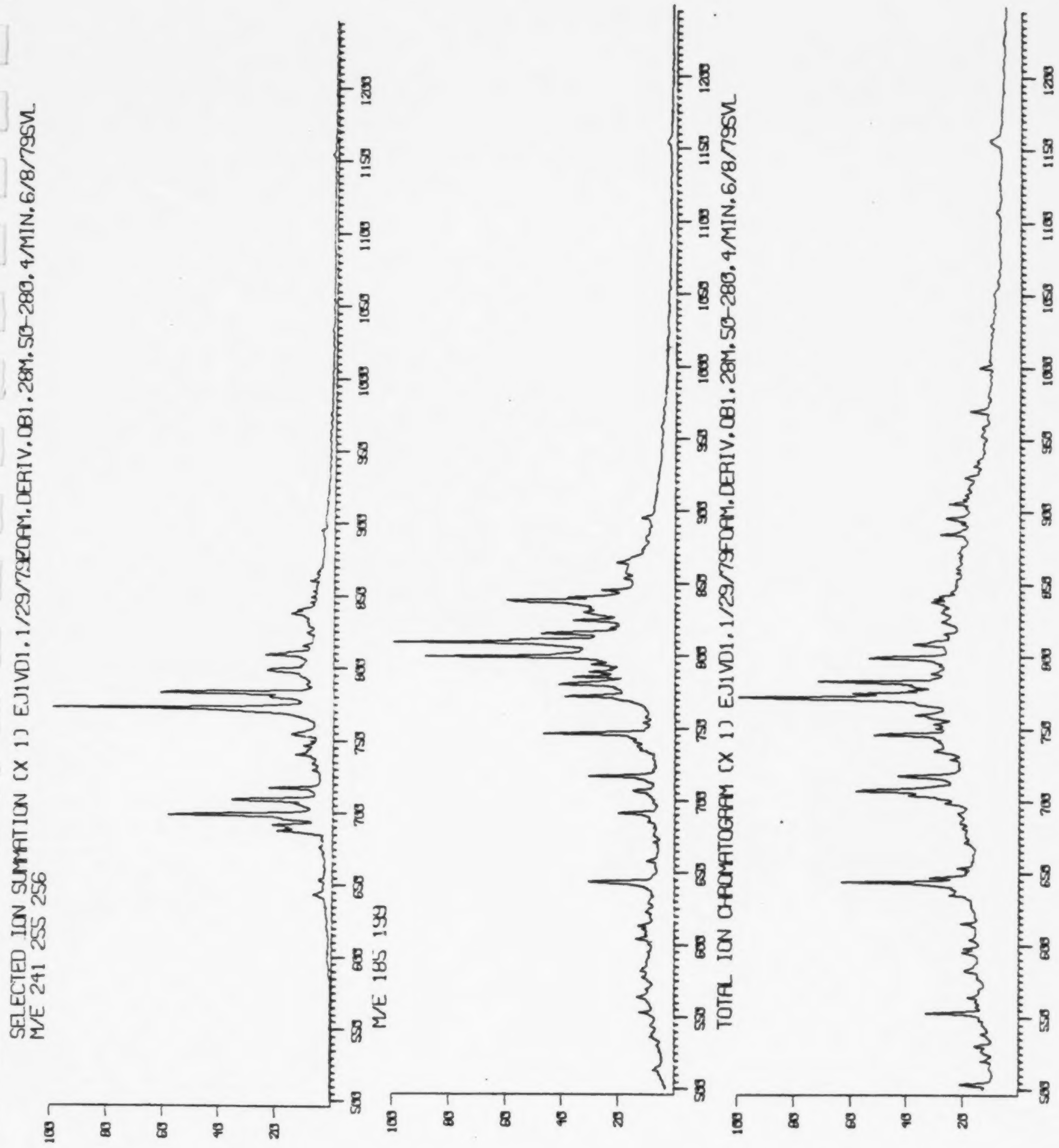


Figure 7. 1/29/79 Sample; Resin Acid Indicator Ions, Specific Ion Chromatograms

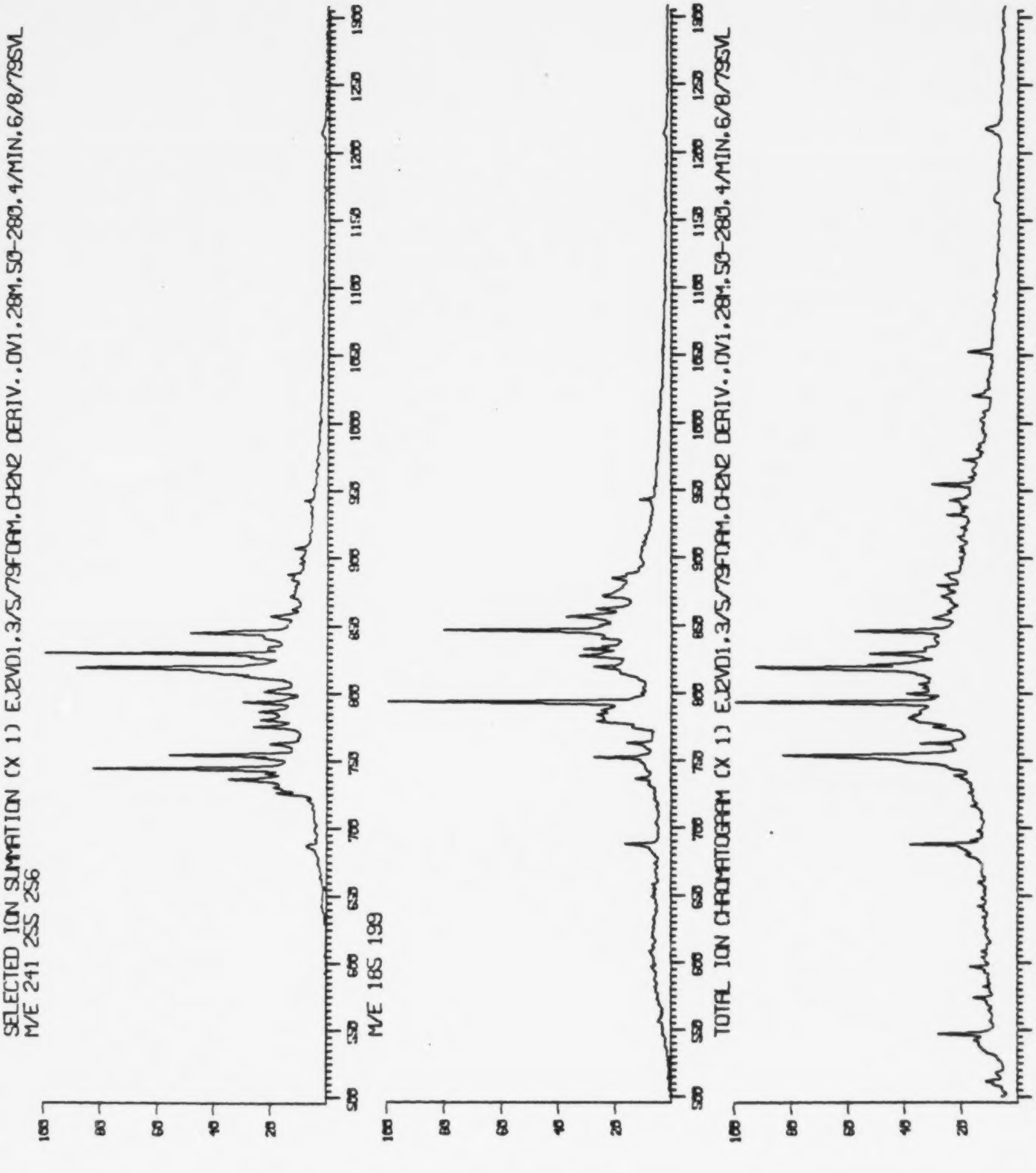
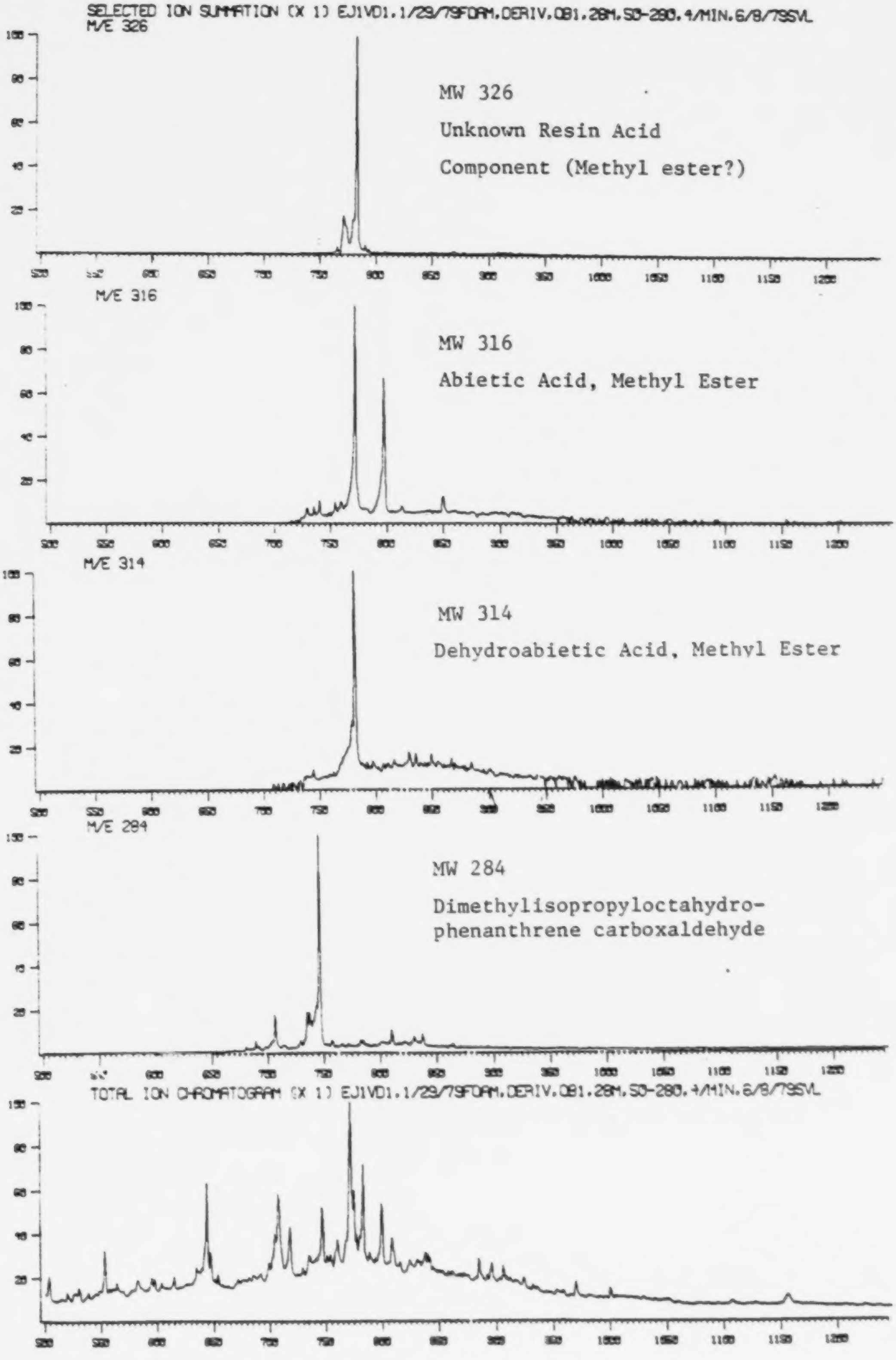


Figure 8. 3/5/79 Sample; Resin Acid Indicator Ions, Specific Ion Chromatograms



MW 326

Unknown Resin Acid

Component (Methyl ester?)

MW 316

Abietic Acid, Methyl Ester

MW 314

Dehydroabietic Acid, Methyl Ester

MW 284

Dimethylisopropyloctahydro-
phenanthrene carboxaldehyde

Figure 9. 1/29/79 Sample, Ion Chromatograms for Selected Molecular Weights of Resin Acid Species

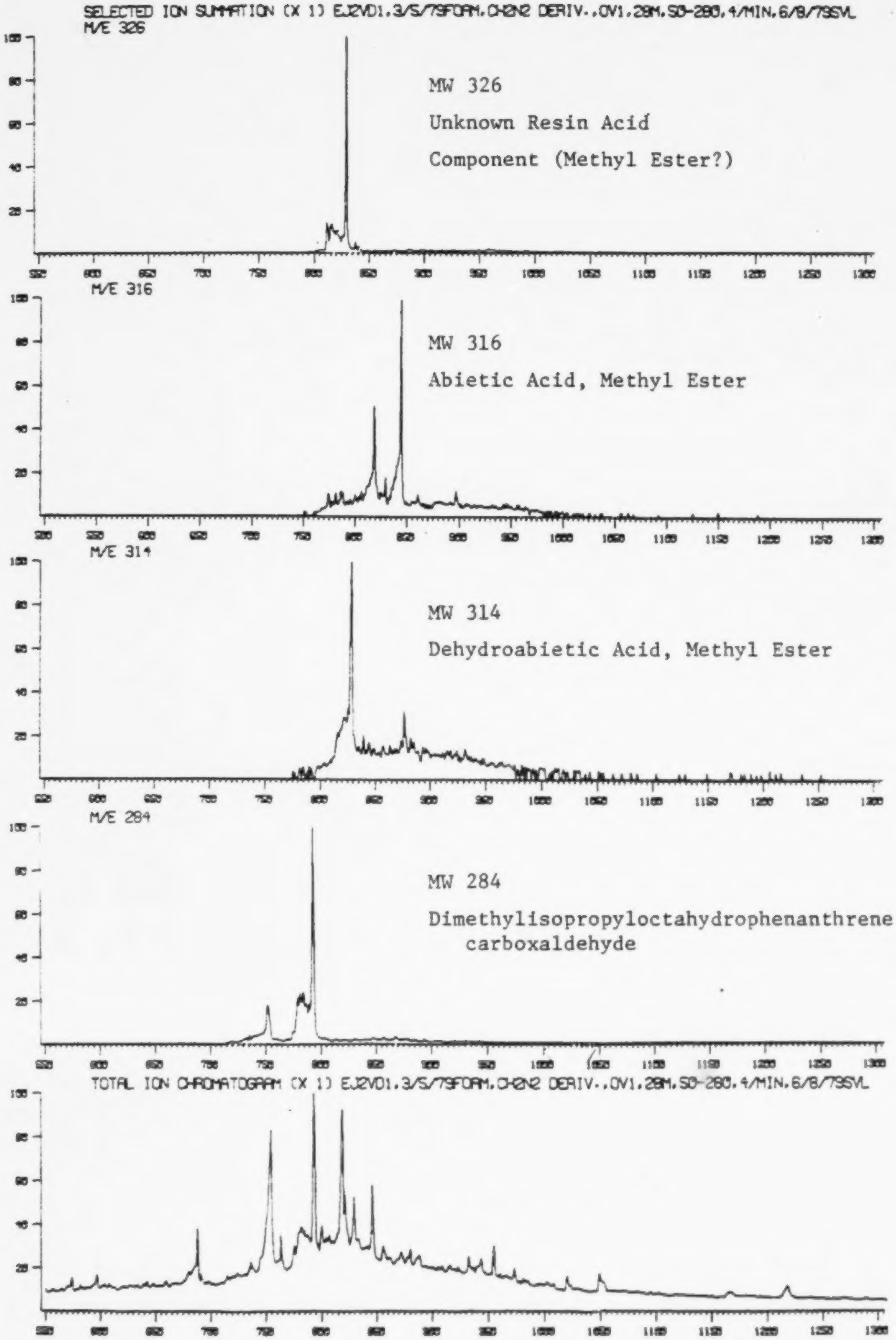


Figure 10. 3/5/79 Sample; Ion Chromatograms for Selected Molecular Weights of Resin Acid Species

EXPERIMENTAL

Anthrone Test

The total carbohydrate content was determined for a 2 ml aliquot of the foam sample using the procedure of Viles and Silverman (Analytical Chemistry, 21, 950 [1949]). The response was compared to a 50 ppm cellulose solution, which gave good response. However, the sample itself gave a very low absorbance indicating that < 10 mg/l of carbohydrates are present.

Cellulose Digestion

An enzymatic hydrolysis of the collapsed foam was made using conditions approximating those found in the literature[*]. A 2.0 ml aliquot of the effluent was adjusted to pH 4.8 using concentrated HOAc and NaOAc, 200 mg of cellulase was added to the effluent and a distilled water blank, and both samples were hydrolyzed at 40 C for 48 hours. After hydrolysis, the samples, along with a 2.0 ml aliquot of the non-hydrolyzed effluent (pH=4.8) were centrifuged at 1850 rpm on a clinical centrifuge, and a 1.0 ml aliquot of each was taken for CHO analysis according to the procedure of N. Patil, et al (Carbohydrate Research, 29, 513-519 [1973]). This procedure uses the complex formed from thymol-ferric chloride-hydrochloric acid with absorbance measurements at 625 nm for quantitation. Cellulose was used as standard.

All samples containing cellulase read very high in carbohydrate, with both blanks giving higher absorbances than the hydrolyzed effluent. Apparently, the cellulose preparation we used gives too high a background for this procedure, and therefore, interferes with the carbohydrate test.

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[*] Enzymatic Degradation of Cellulose Fibers, J. Polymer Sci, Part C, 28, 197-207, (1969)

Methylene Blue Active Substances (MBAS)

A portion of the pulp mill effluent was analyzed for alkyl benzene sulfonates using the ASTM Standard Test (Designation D2330-68). The standard for these analyses was sodium dodecyl benzene sulfonate. The procedure used was method A, the Direct Methylene Blue Colorimetric Test, adapted from "Surfactants (Anionic); Methylene Blue Methods" - Standard Methods for the Examination of Water and Wastewater, 12th Edition, 1965. The sample was analyzed by standard addition, with the addition of 5.0 ml of 0.01 mg/ml standard to 10.0 ml of effluent, using distilled water as the blank. Approximately 46ppm of MBAS (as sodium dodecyl benzene sulfonate) was present in the sample.

TOC Analyses in Pulp Mill Effluent After n-butanol Extraction

50ml of pulp mill effluent was extracted twice with 50 ml of H_2O-equilibrated, distilled in glass, n-butanol.

The n-butanol was evaporated to dryness in a centrifuge tube on a vortex evaporator. The dried sample was dissolved in 5.0 ml of distilled water for TOC analysis.

The extracted effluent (50ml) was also dried and redissolved in distilled H_2O (50ml) and TOC analyses done. A blank of 50 ml distilled H_2O was treated similarly.

The TOC in the butanol extract was 20ppm (normalized to the amount of original sample extracted) and the TOC in the remaining water was 58 ppm. Since the original TOC of the water was 490 ppm this result was rather disturbing, since only = 78 ppm was recovered.

The order to determine if some of the TOC was volitile the sample (10 ml) was evaporated just to dryness at 50° on a rotating evaporator and then redissolved in distilled water. This sample contained only 60 ppm of TOC. A second 10 ml aliquot was evaporated to 5 ml, diluted to 10 ml with distilled water and analyzed. It was found to contain 170 ppm. The unconcentrated sample was reanalyzed and found to contain 610 ppm.

These results lead us to the conclusion that a large majority of the TOC in the extracted sample is volitile material, perhaps residual extraction solvent or water soluable impurities in the solvent.

ATTACHMENT A

18 JUNE 79 REPORT

CHARACTERIZATION OF THE NONEXTRACTABLE ORGANIC MATERIALS IN RIVER FOAM

INTRODUCTION

The following work was directed toward the characterization of nonextractable organics from foam collected from a river which receives pulp mill effluent. The experimental methods consisted of size separation of the effluent using gel filtration chromatography followed by analysis of the various size fractions for phenol, carbohydrate and nitrogen content. The effluent was also examined after acid hydrolysis.

EXPERIMENTAL

The scheme utilized for the characterization of the effluent is shown in Figure 1.

The aqueous sample received contained insoluble particulate and methylene chloride ($MeCl_2$). After removal of the $MeCl_2$ using a separatory funnel, an aliquot of the sample was analyzed for total organic carbon (TOC). The remainder of the sample was adjusted to pH 7 to dissolve some of the particulate matter and reanalyzed for TOC. (Both samples were heated at 60°C for 30 minutes to remove dissolved $MeCl_2$ prior to TOC analysis.)

The aqueous sample was chromatographed using a 2.5 cm x 45 cm column (bed volume equal to 260 milliliters) packed with Sephadex G-25-150 and a mobile phase of 50% aqueous actone.

Catechin (M.W. ~400) and tannic acid (M.W. ~1000) were used to calibrate the chromatographic system so that three molecular weight (M.W. ~400) fractions could be collected:

Fraction 1	60-90 milliliters	>1000 M.W.
Fraction 2	90-110 milliliters	400 - 100 M.W.
Fraction 3	110-150 milliliters	<400 M.W.

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Three milliliters of the aqueous effluent were fractionated for each characterization study. Each size fraction and an unfractionated sample were analyzed using Folin and Ciocalteus' reagent for phenols, thymol-ferric chloride-hydrochloric reagent for carbohydrates and Kjeldahl-N method for nitrogen.

For the determination of phenolic content, each M.W. fraction was concentrated to 3 milliliters (mls) with a rotary evaporator (70°C). One milliliter (ml) of each fraction and 1 ml of the unfractionated effluent were combined with 1 ml of Folin and Ciocalteus phenol reagent and 10 mls of 1% sodium tartrate in 20% Na_2CO_3. After sitting at room temperature for 30 minutes, the solutions developed a blue color, the absorbance of which was monitored from 663 nm.

For carbohydrate analysis, each M.W. fraction was reduced to half its original volume with a rotary evaporator (30°C). Ten milliliters of each size fraction and 10 mls of the unfractionated effluent were combined with 500 microliters of 5% thymol in ethanol (ETOH) and 5 ml of 0.5% ferric chloride in concentrated HCl. The mixtures were heated on a boiling water bath for 60 minutes, cooled to room temperature, and then diluted to 10 mls with ETOH. With the addition of ETOH the solutions became a green color, the absorbance of which was determined at 634 nm. Standards of D-glucose were used as a quantitative reference.

Protein content was determined using Kjeldahl-Nitrogen methodology. Each M.W. fraction was concentrated to half its original volume prior to analysis. Ten milliliters of each fraction and the nonfractionated effluent were combined with 1.5 K_2SO_4, 10-15 milligrams $CuSeO_4 \cdot 4H_2O$ and 3 mls concentrated H_2SO_4 and heated until the bulk of H_2O was removed. The reaction mixture was then heated for 30 minutes past the fuming point of H_2SO_4. The mixture was cooled, 1 ml of H_2O_2 added and then reheated for 30 minutes (to remove excess of H_2O_2). The reaction mixture was transferred to a distillation apparatus to which 25 ml of NaOH solution (prepared by dissolving 340 g NaOH in 1000 ml·H_2O, adding 0.5 g Devarda's alloy and boiling until the volume is about 900 ml) was added. The distillate was titrated with 0.007N H_2SO_4.

A portion of the aqueous effluent (pH 7) was hydrolyzed by adding 6 N HCl and heating at 90°C for 60 minutes. To determine the presence of hydrolyzable components, part of the acid hydrolyzed material was extracted with $MeCl_2$. TOC analyses were then conducted on the extracted and non-extracted hydrolyzed sample.

The acid hydrolyzed sample was chromatographed and characterization studies were conducted on each of the size fractions as described above.

RESULTS AND CONCLUSIONS

The aqueous phase, at pH 2, was found to contain 360 mg/liter of TOC. After adjustment to pH 7 TOC was found to be 490 mg/liter. This finding demonstrates that some of the suspended material dissolved after pH adjustment, and did contribute somewhat to the TOC value.

After acid hydrolysis the TOC value was found to be 690 mg/liter before extraction and 590 mg/liter after extraction with methylene chloride. This finding indicates that acid hydrolysis does not create more extractable organic material. Hydrolysis of phenolic glycosides can result in increased extractability, but this does not appear to be happening to a significant extent for this sample.

The distribution of carbohydrates, phenols, and organic nitrogen in various fractions is shown in Table 1. The results for carbohydrates is reported relative to glucose, although this procedure is felt to give uniform response for most carbohydrates. Phenol was used as the reference standard for the Folin's analysis.

Total carbohydrate was found to be approximately 40 mg/l both before and after hydrolysis. Size fractionation indicated that there was a shift of material from the large size fraction to the smaller size fractions upon hydrolysis, thus indicating that some cleavege of phenolic glycosides had occurred. The anomalously high value of 63 mg/l for the first fraction in the unhydrolyzed sample is not as yet understood. The most significant conclusion from these data is that carbohydrates represent a relatively small portion (<4%) of the TOC. We draw this conclusion with some confidence since all carbohydrates give fairly uniform response in the colorimetric test.

Kjeldahl nitrogen content was found to be very low and it is difficult to say anything except that proteins and amino acids do not represent a significant fraction (<1-2%) of the TOC.

Phenol values were 14 mg/liter before hydrolysis and 20 mg/liter after hydrolysis, indicating that some phenolic glycosides were cleaved. Size fractionation indicated that most of the phenolic content is of higher molecular weight and this distribution is not changed by hydrolysis. Phenols appear to represent less than 5% of the total organic carbon. However, the response of the colorimetric tests varies rather widely from compound to compound so that it is difficult to say what the exact levels are.

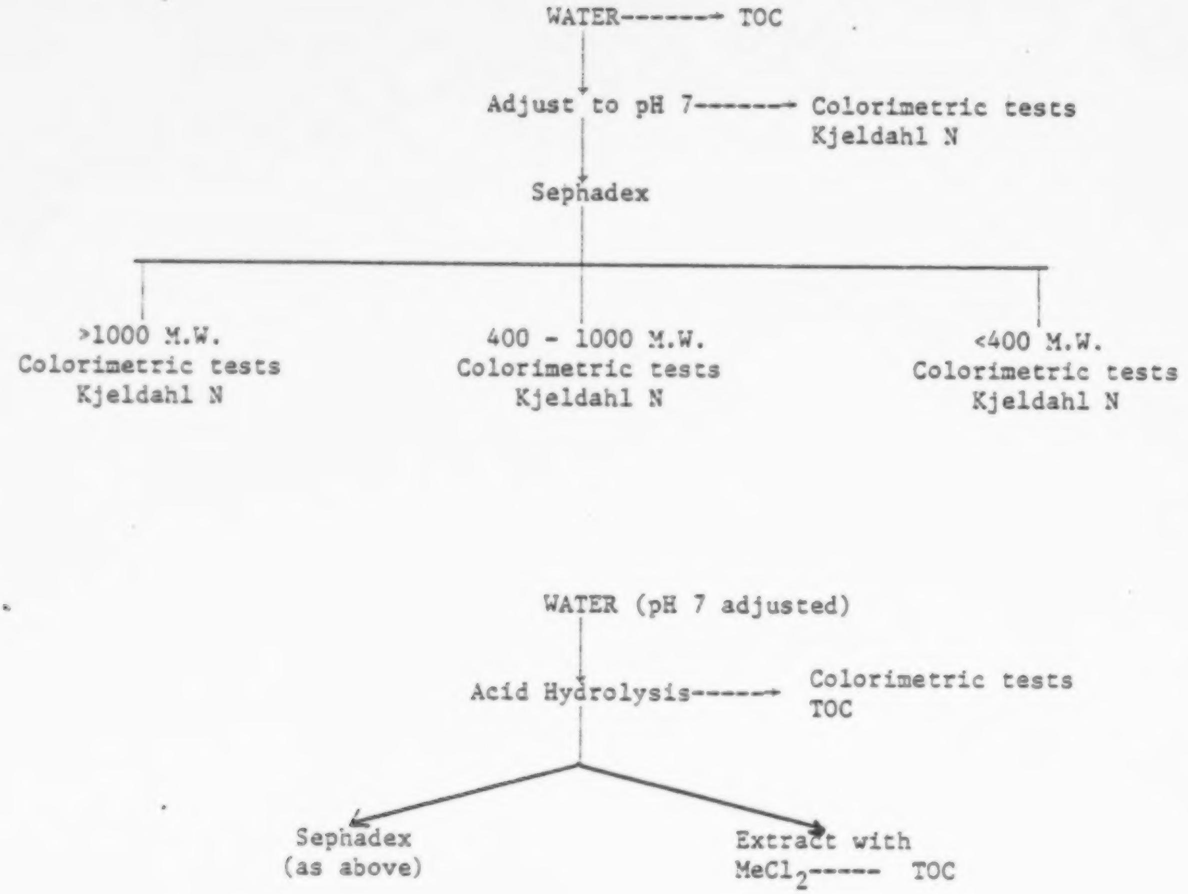

WATER------→ TOC
Adjust to pH 7------→ Colorimetric tests
Kjeldahl N
Sephadex
>1000 M.W.
Colorimetric tests
Kjeldahl N
400 - 1000 M.W.
Colorimetric tests
Kjeldahl N
<400 M.W.
Colorimetric tests
Kjeldahl N
WATER (pH 7 adjusted)
Acid Hydrolysis-----→ Colorimetric tests
TOC
Sephadex
(as above)
Extract with
MeCl2----- TOC

FIGURE 1. CHARACTERIZATION SCHEME FOR PULP MILL EFFLUENT

TABLE 1. ORGANIC CONTENT IN AQUEOUS EFFLUENT

		Aqueous Effluent milligram/liter	Hydrolyzed Aqueous Effluent milligram/liter
Carbohydrate content			
	nonfractionated	38.9	42.1
	>1000 M.W.	63.0	24.2
	400 - 1000 M.W.	<5.0	9.3
	<400 M.W.	12.3	18.2
Nitrogen content			
	nonfractionated	2.1	did not analyze
	>1000 M.N.	1.0	1.0
	400 1000 M.W.	1.0	0.7
	<400 M.W.	0.7	0.7
Phenolic content			
	nonfractionated	14.6	20.2
	>1000 M.W.	23.8	12.2
	400 - 1000 M.W.	0.4	0.4
	<400 M.W.	5.1	2.3

SUGGESTIONS FOR FURTHER WORK

GC-MS analysis of the 1/29/79 and 3/5/79 extracted foam samples has provided a good deal of information about the types of chemical species present in this material. The data also clearly indicates a number of refinements in the analytical scheme which can be expected to provide even more information from the next set of samples.

The samples are extremely complex, and greater chromtographic separation would result in "cleaner" mass spectra and better performance of the computer mass spectral library system. The following modifications can be expected to provide the improved separation:

1. Chromatographic temperature programming was begun at 50°C to enable analysis of the "Consent Decree" phenols. Since no "Consent Decree" phenols or simple components of any significance were detected at these lower temperatures, a high initial temperature and much slower temperature programming rate (1° or 2°/min) will effect better separation of the late-eluting "hump".
2. Many sample components were detected which did not have an acidic functionability. A prior cleanup step to partition the acids into aqueous base would simplify analysis of these neutral compounds greatly.
3. Since the sample seems to contain a number of fatty substituted phenols--possibly arising from lignin--which do not methylate with diazomethane, a post-derivitization partitioning between a very non-polar solvent (hexane?) and aqueous base might separate the methylated carboxylic acids and free phenols into two more analyzable fractions.

It is suggested that some of the above techniques be tried on just one or two samples to evaluate the merits and refine the procedure.

APPENDIX 1

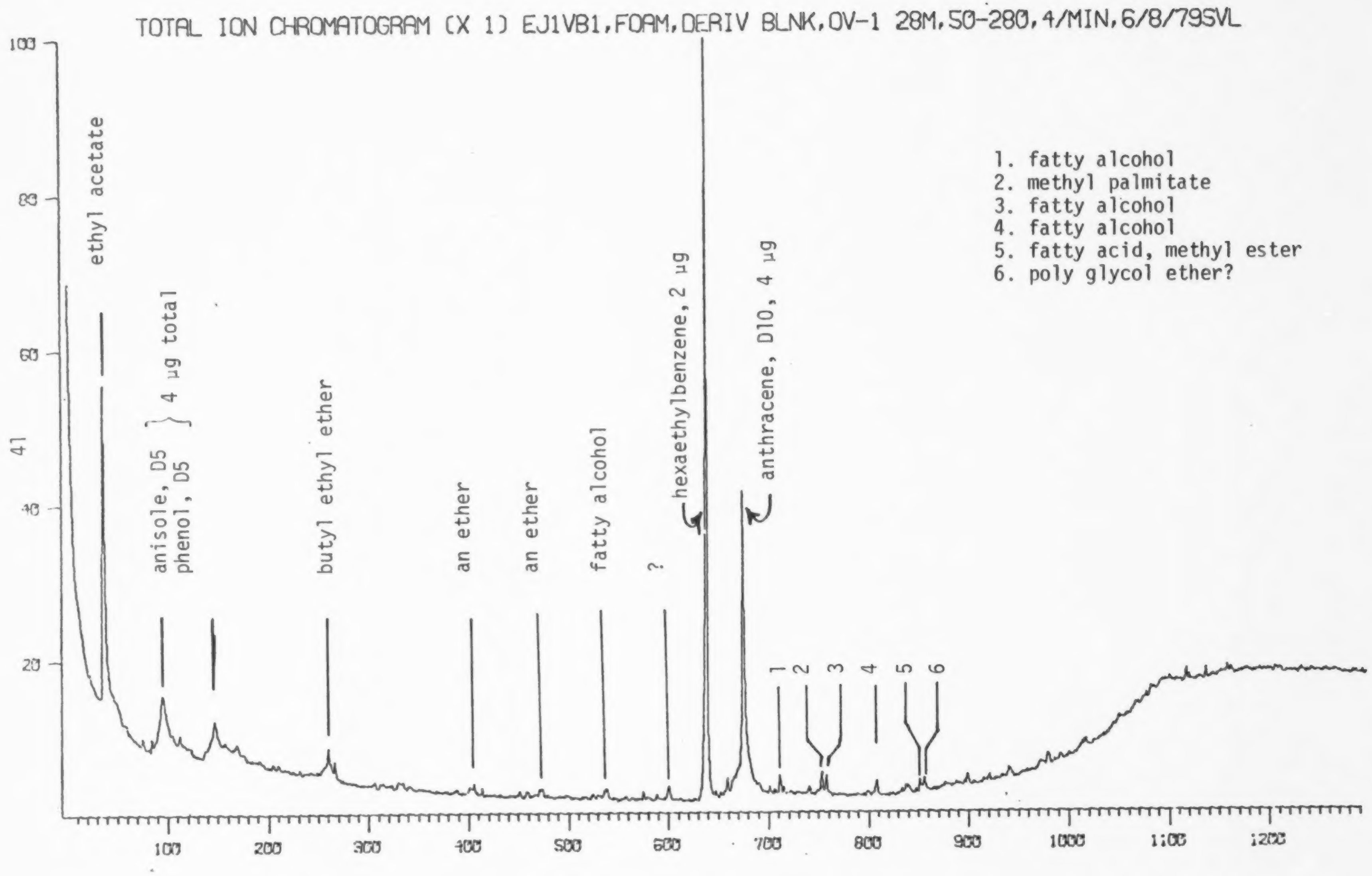


FIGURE 1. DIAZOMETHANE DERIVATIZATION BLANK

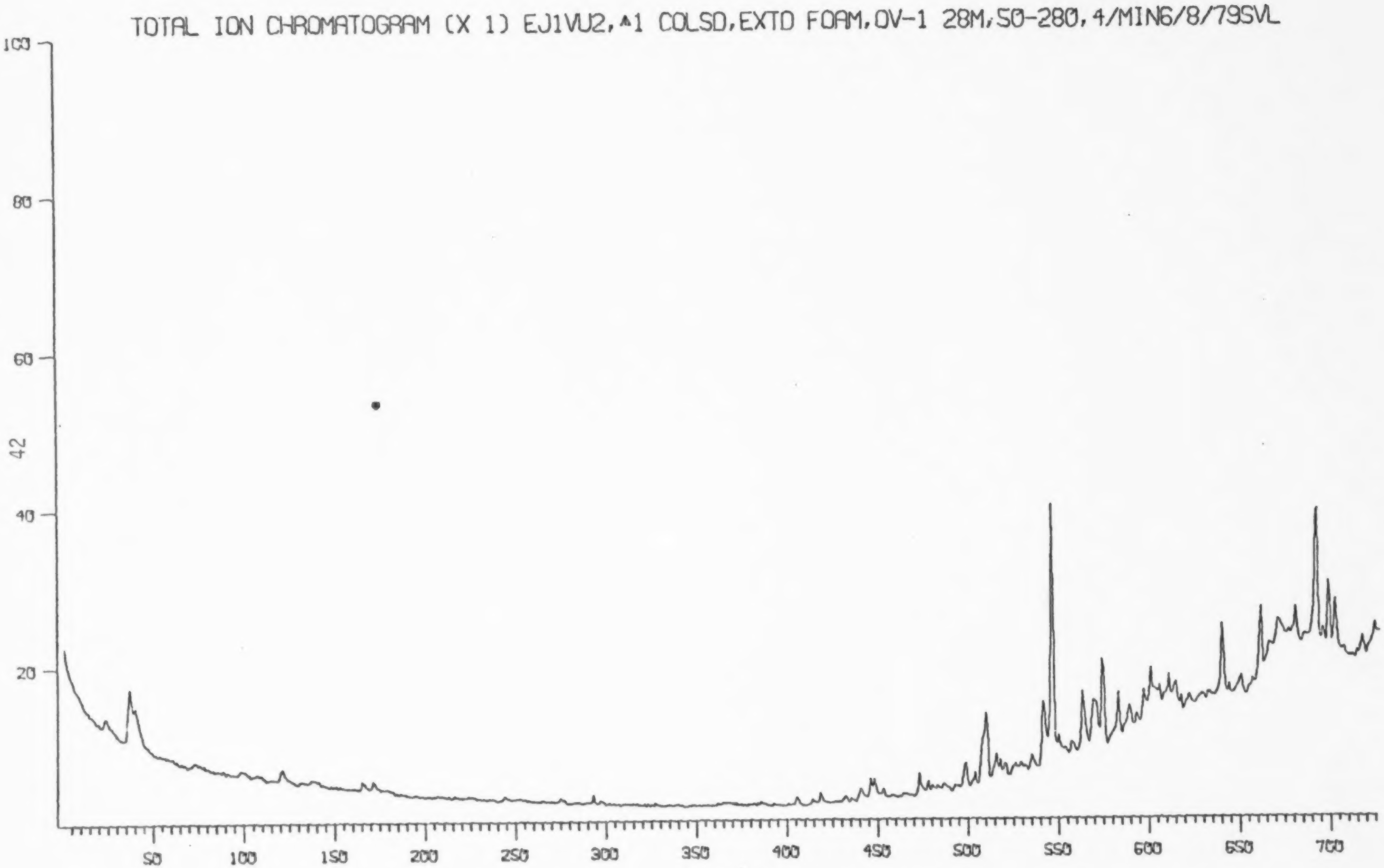


FIGURE 2. 1/29/79 SAMPLE, UNDERIVATIZED, AS RECEIVED

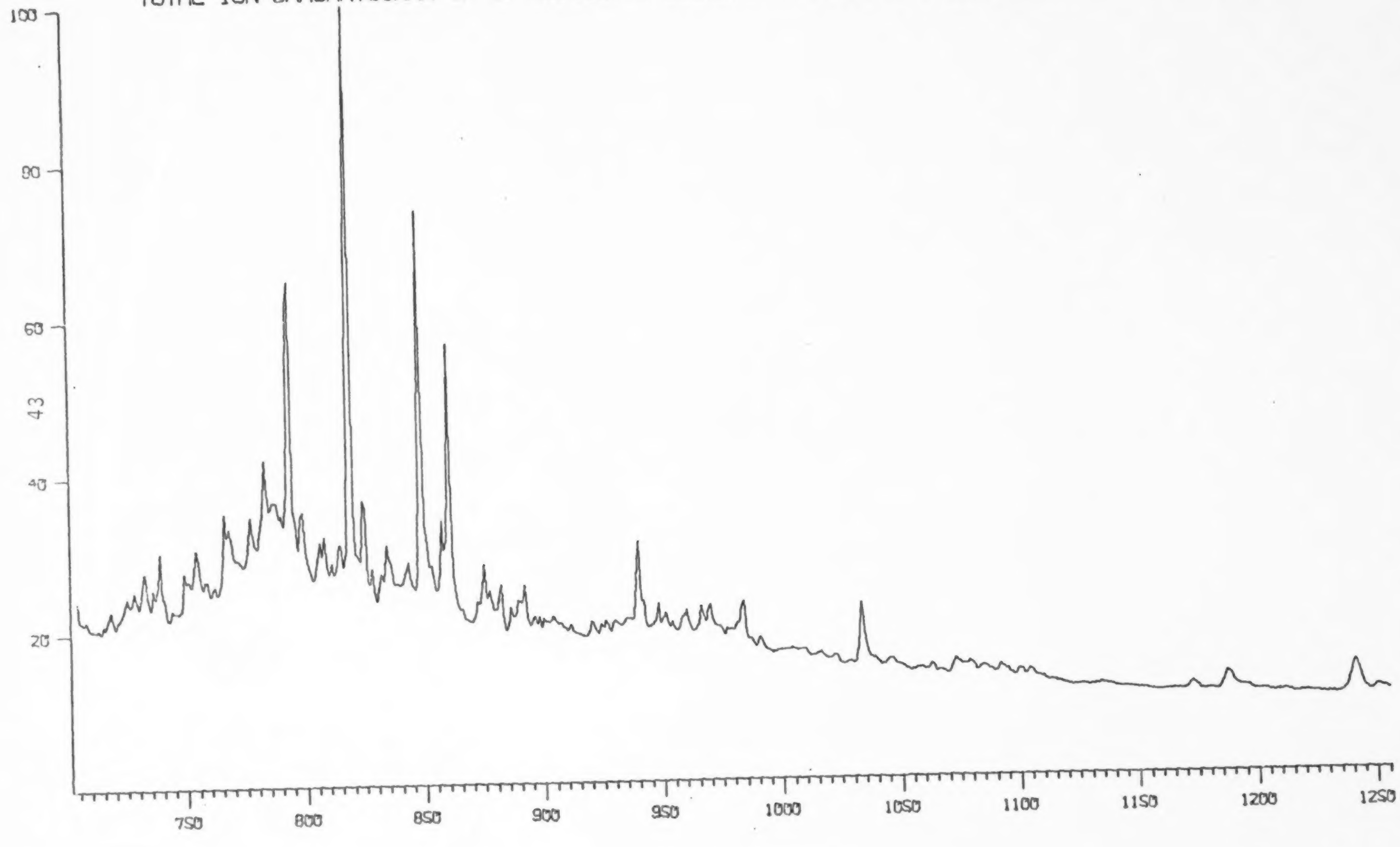

TOTAL ION CHROMATOGRAM (X 1) EJ1VU2,▲1 COLSD,EXTD FOAM,OV-1 28M,50-280,4/MIN6/8/79SVL

FIGURE 2. CONTINUED

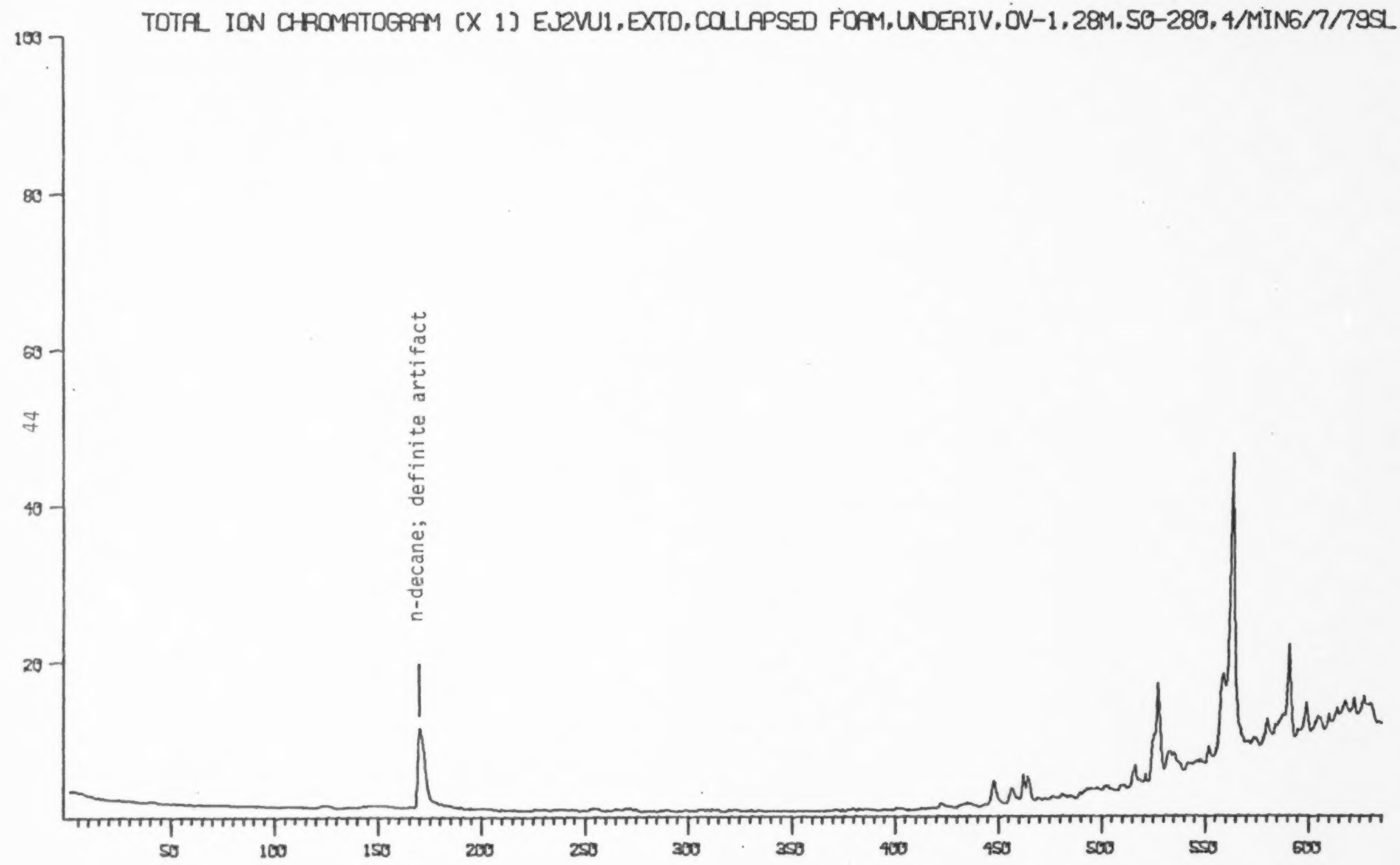


FIGURE 3. 3/5/79 SAMPLE, UNDERIVATIZED, AS RECEIVED

TOTAL ION CHROMATOGRAM (X 1) EJ2VU1,EXTD,COLLAPSED FOAM,UNDERIV,OV-1,28M,50-280,4/MIN6/7/79SL

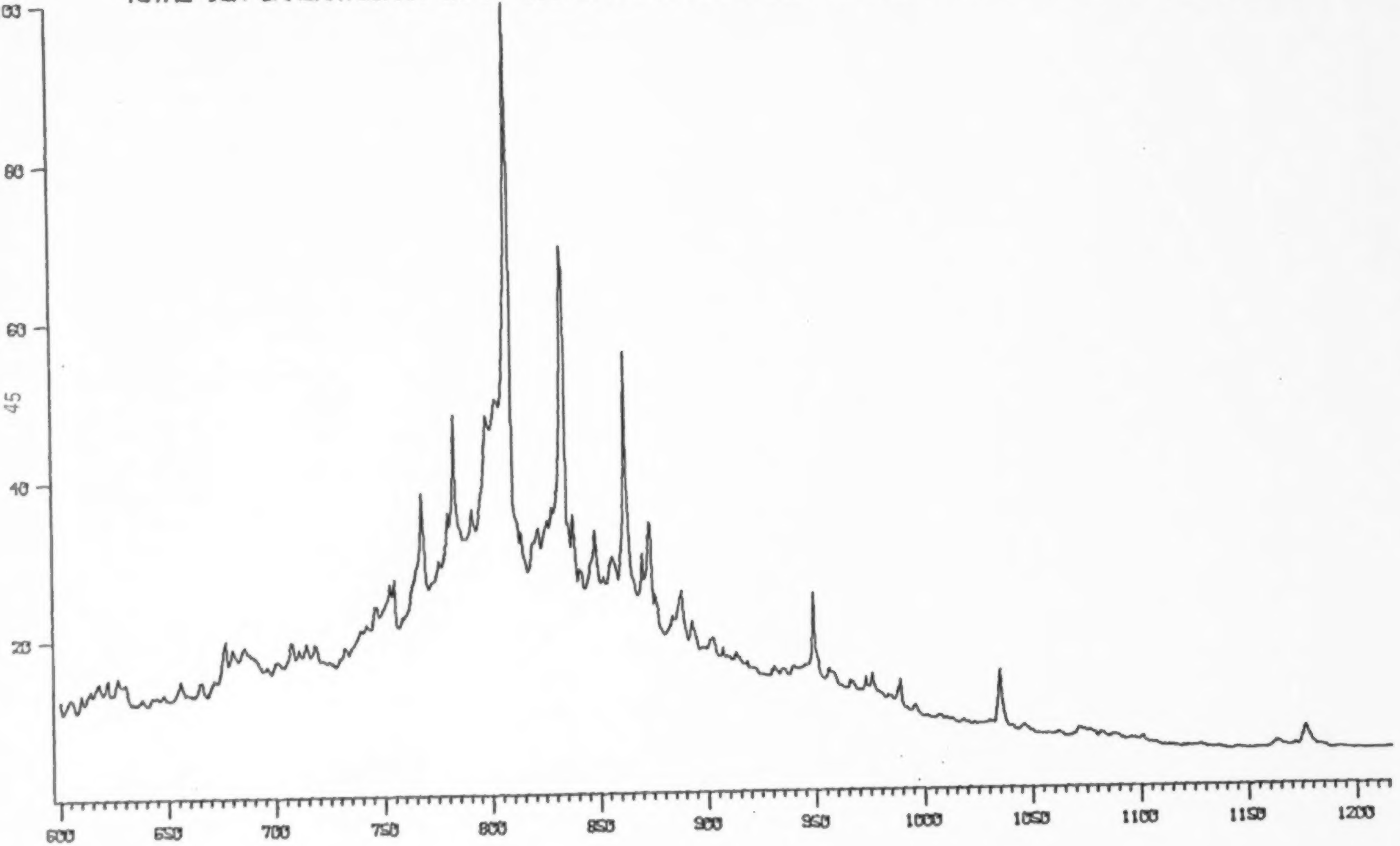


FIGURE 3. CONTINUED

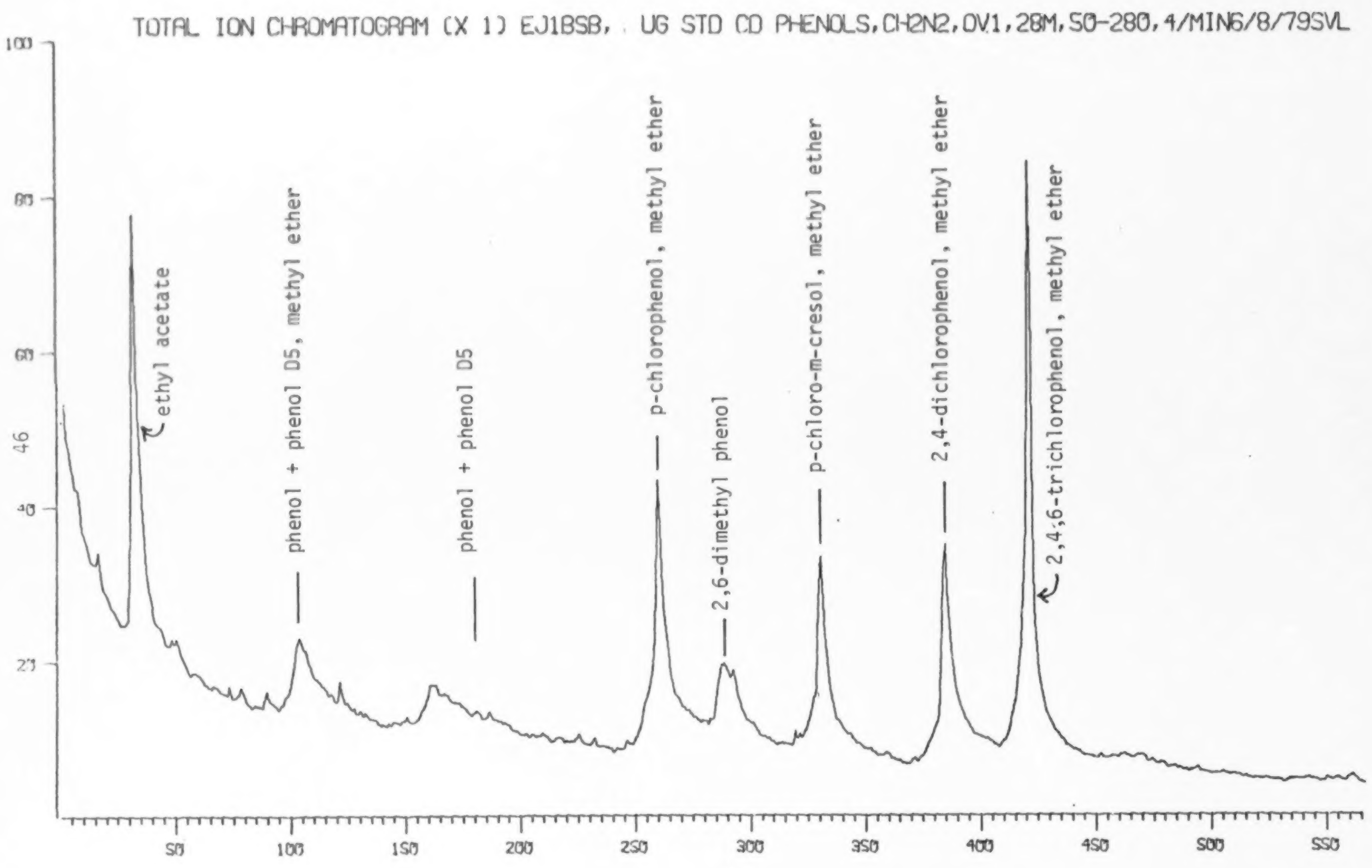


FIGURE 4. PHENOL STANDARDS, 1.5 μg EACH, "CONSENT DECREE" PHENOLS, SUPELCO, DIAZOMETHANE DERIVATIZED

TOTAL ION CHROMATOGRAM (X 1) EJ1BSB, UG STD CD PHENOLS,CH2N2,OV1,28M,50-280,4/MIN6/8/79SVL

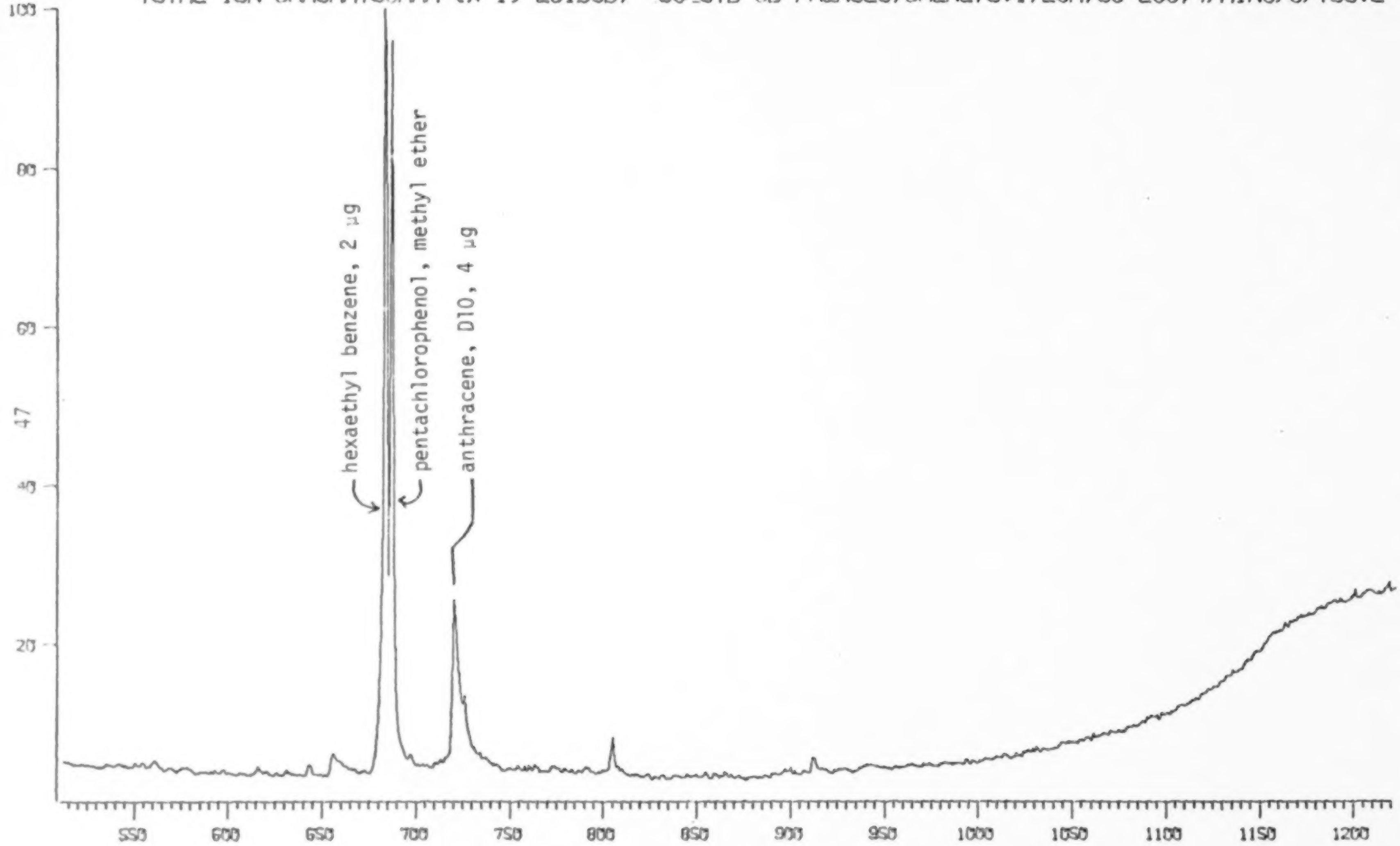


FIGURE 4. CONTINUED

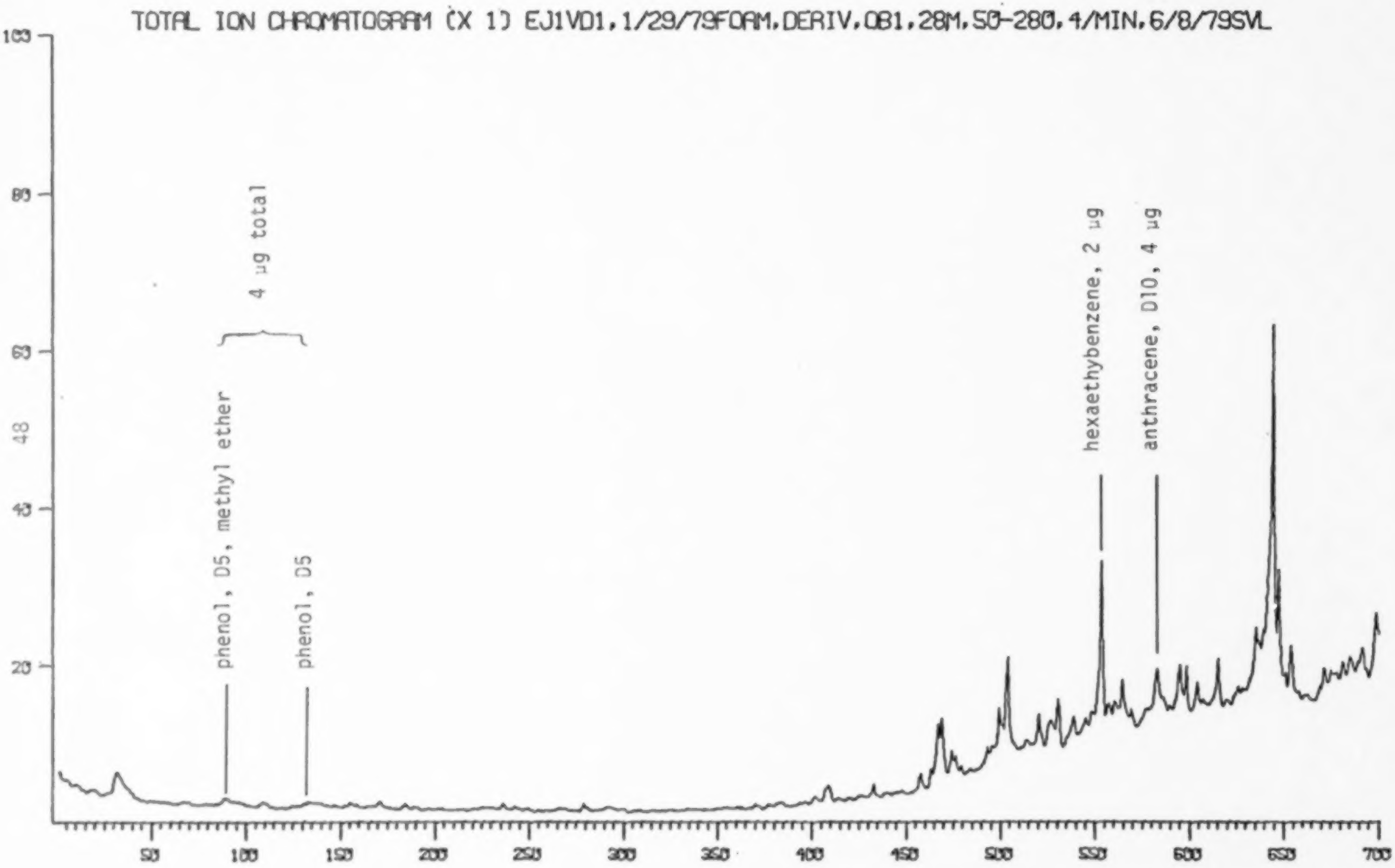

TOTAL ION CHROMATOGRAM (X 1) EJ1VD1,1/29/79FORM.DERIV,OB1,28M,50-280,4/MIN,6/8/79SVL

FIGURE 5. 1/29/79 SAMPLE; DIAZOMETHANE DERIVATIZED

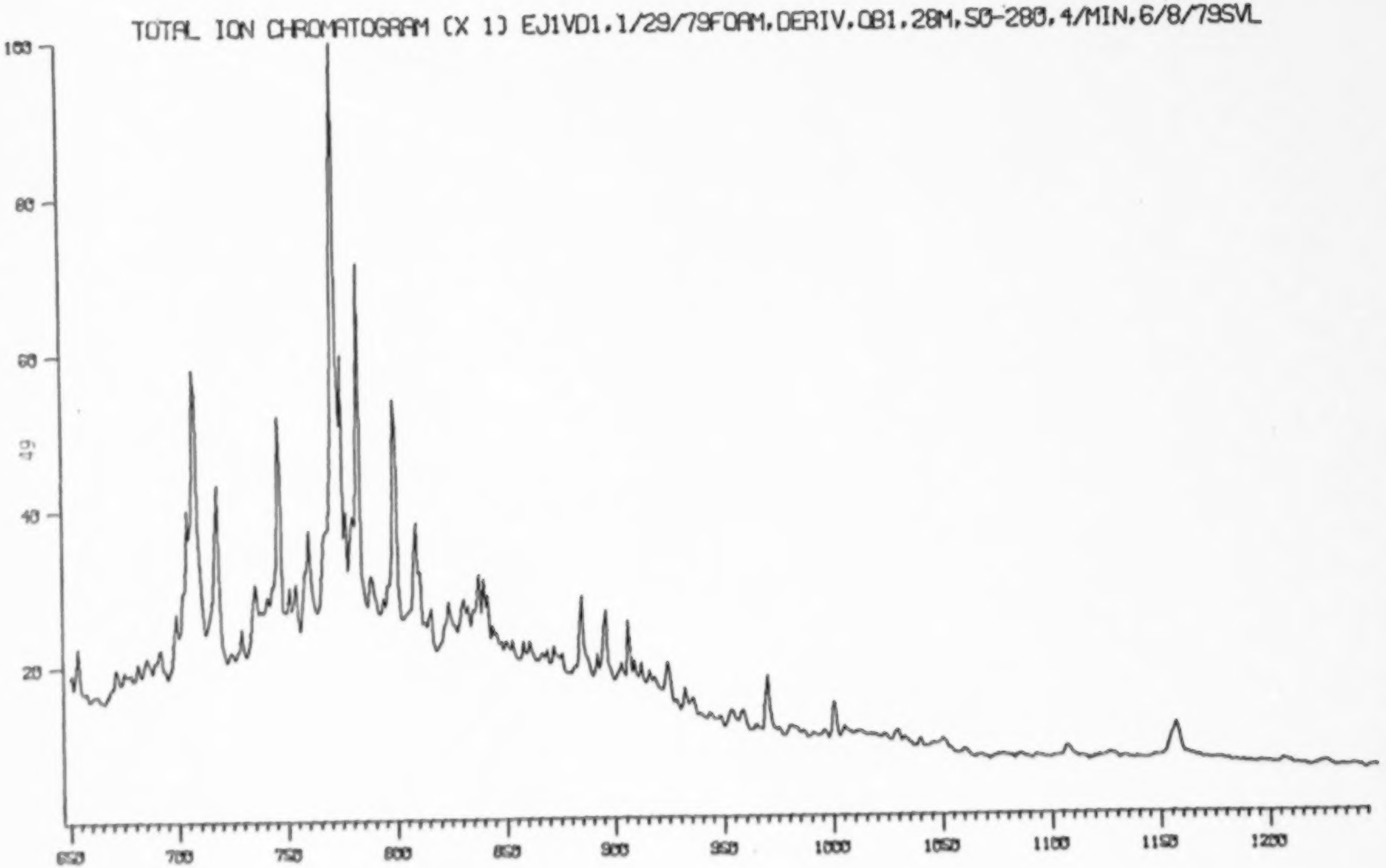


FIGURE 5. CONTINUED

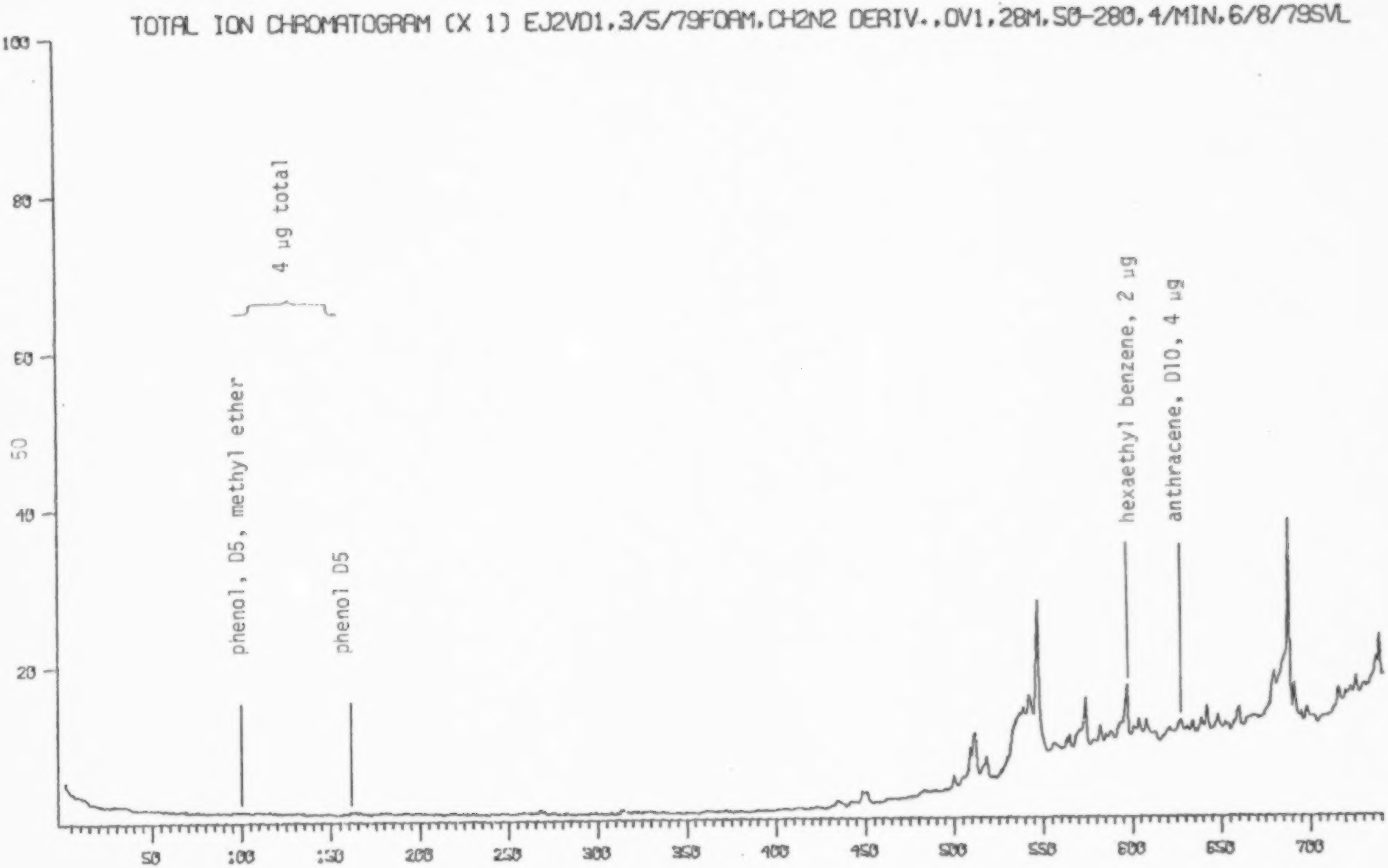


FIGURE 6. 3/5/79 SAMPLE, DIAZOMETHANE DERIVATIZED

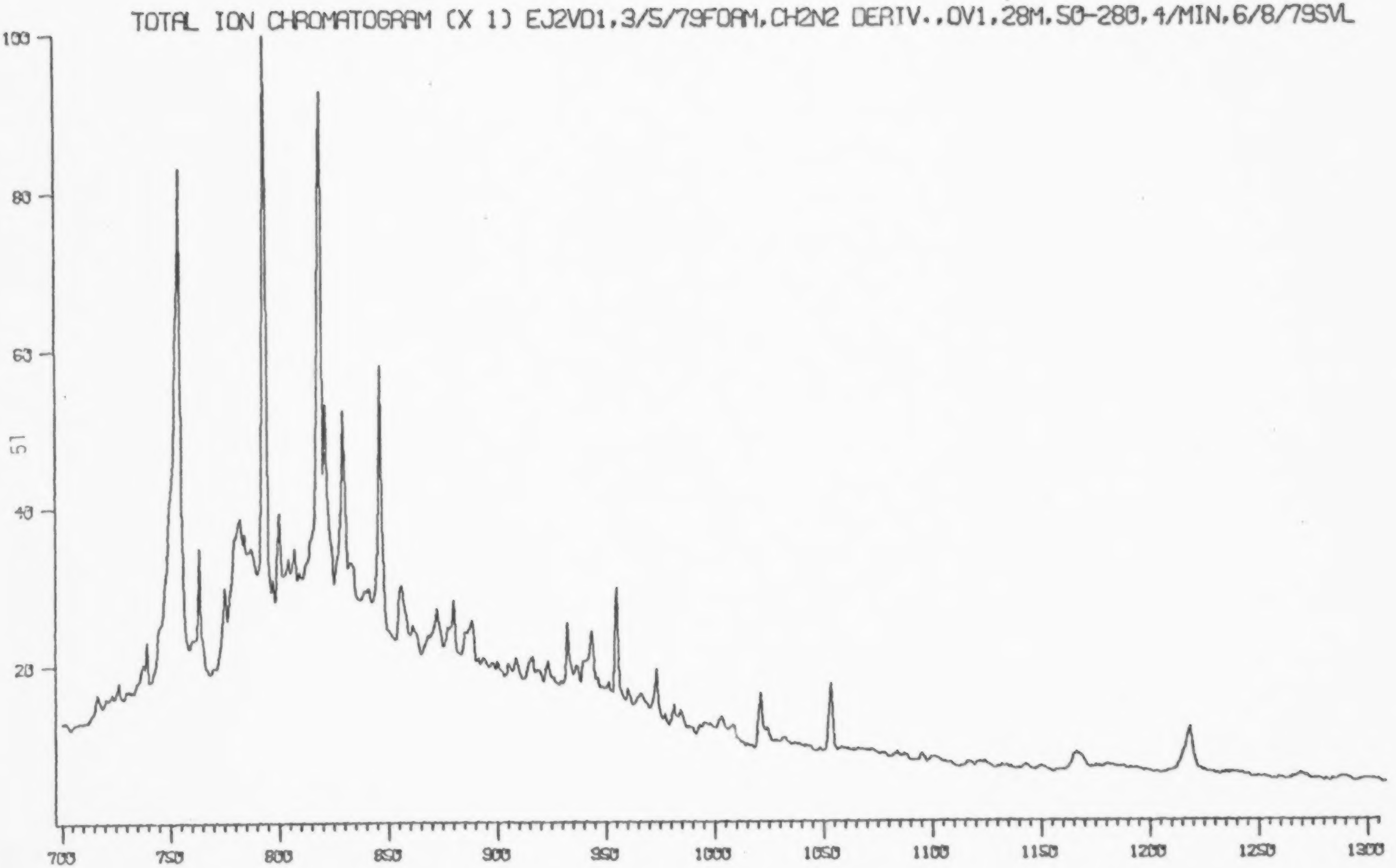


FIGURE 6. CONTINUED

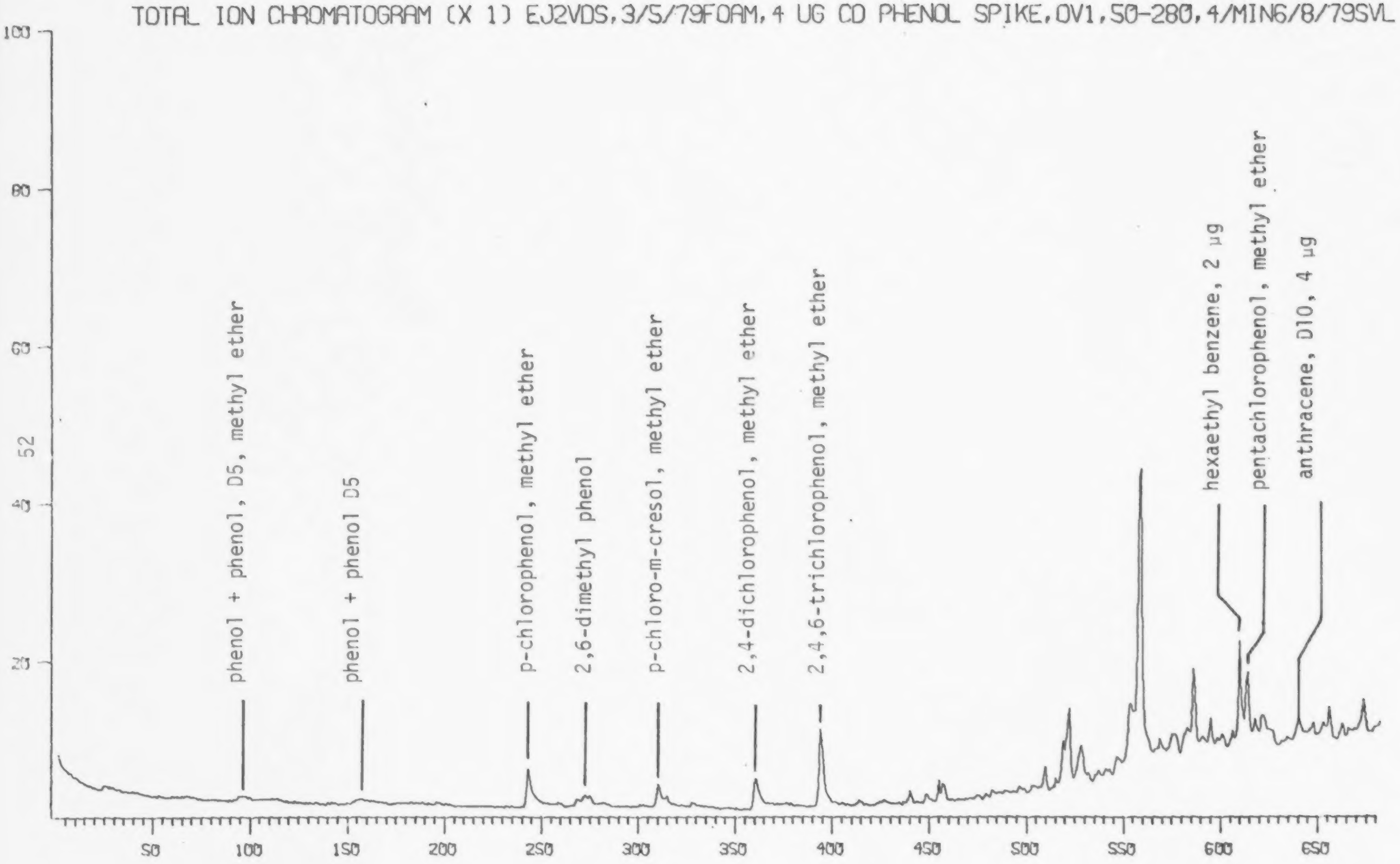


FIGURE 7. 3/5/79 SAMPLE, WITH "CONSENT DECREE" PHENOL SPIKE, 4 μg; DIAZOMETHANE DERIVATIZED

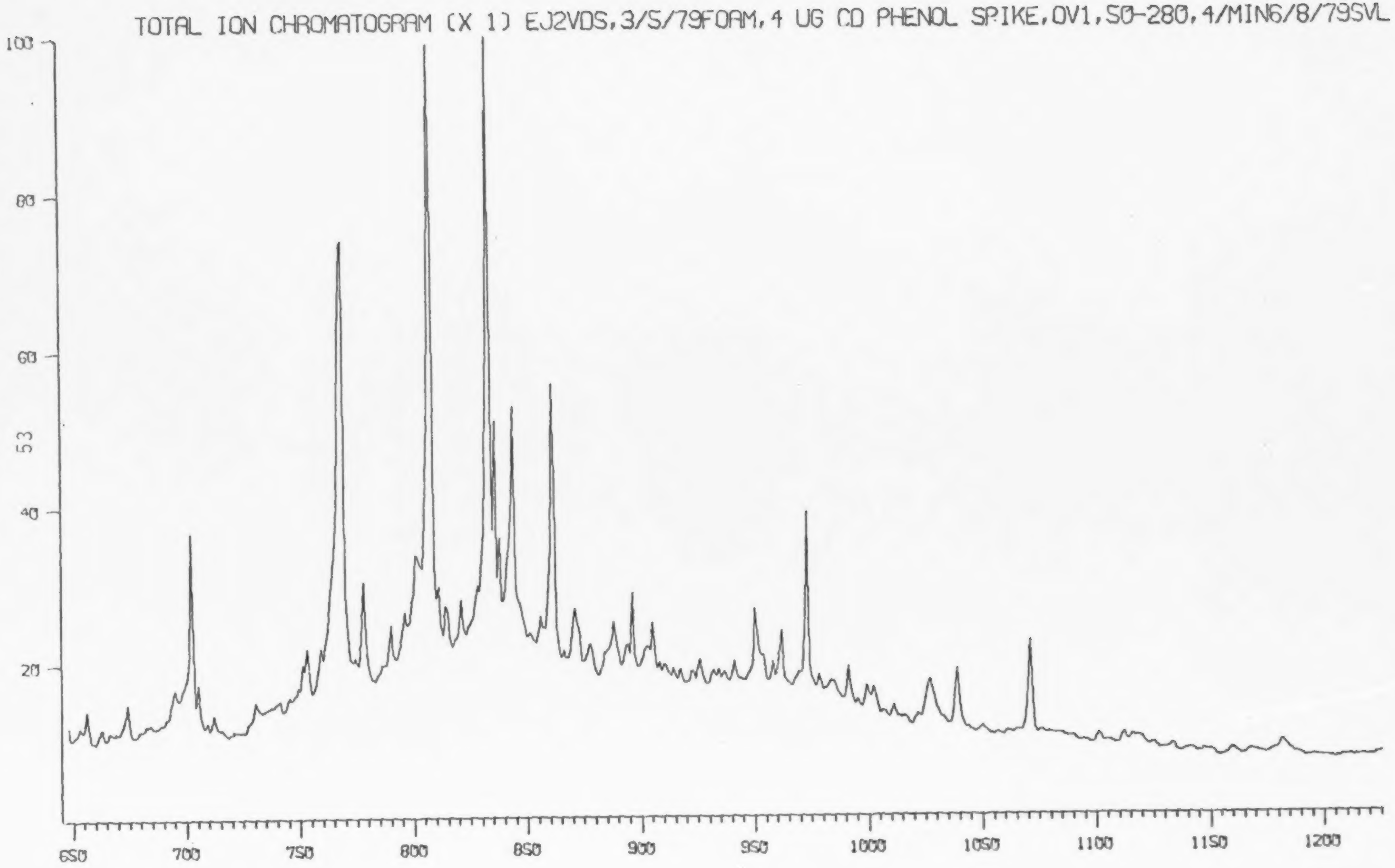


FIGURE 7. CONTINUED

Battelle
Columbus Laboratories
505 King Avenue
Columbus, Ohio 43201
Telephone (614) 424-6424
Telex 24-5454

June 24, 1980

Dr. Bruce K. Wallin
Edward C. Jordan Co., Inc.
PO Box 7050 Downtown Station
Portland, Maine 04112

Dear Dr. Wallin:

Contract No. 68-03-2659

This letter is to summarize the results of work performed as discussed in your letter dated December 31, 1979.

We plan to call you in a few days for further discussions regarding these results and implications for the future.

Outline of the Work Performed

I. Performance validation of the 30-meter SE-52 glass capillary column used for $(GC)^2$-MS and $(GC)^2$-FID analysis.

II. Fractionation of the March 5, 1979 foam sample as described in our scheme in our letter of December 14, 1979.

III. $(GC)^2$-FID analysis and residue weight analysis of samples and blanks for II above.

IV. $(GC)^2$-MS analysis of selected samples from II, above; computerized data reduction; manual data interpretation, as required.

V. $(GC)^2$-FID analysis and residue weight analysis of the "Dam" No. 2 and No. 3 samples.

VI. $(GC)^2$-MS analysis of commercially obtained standards of the resin and selected fatty acids (as methyl esters) which are presently available.

Results

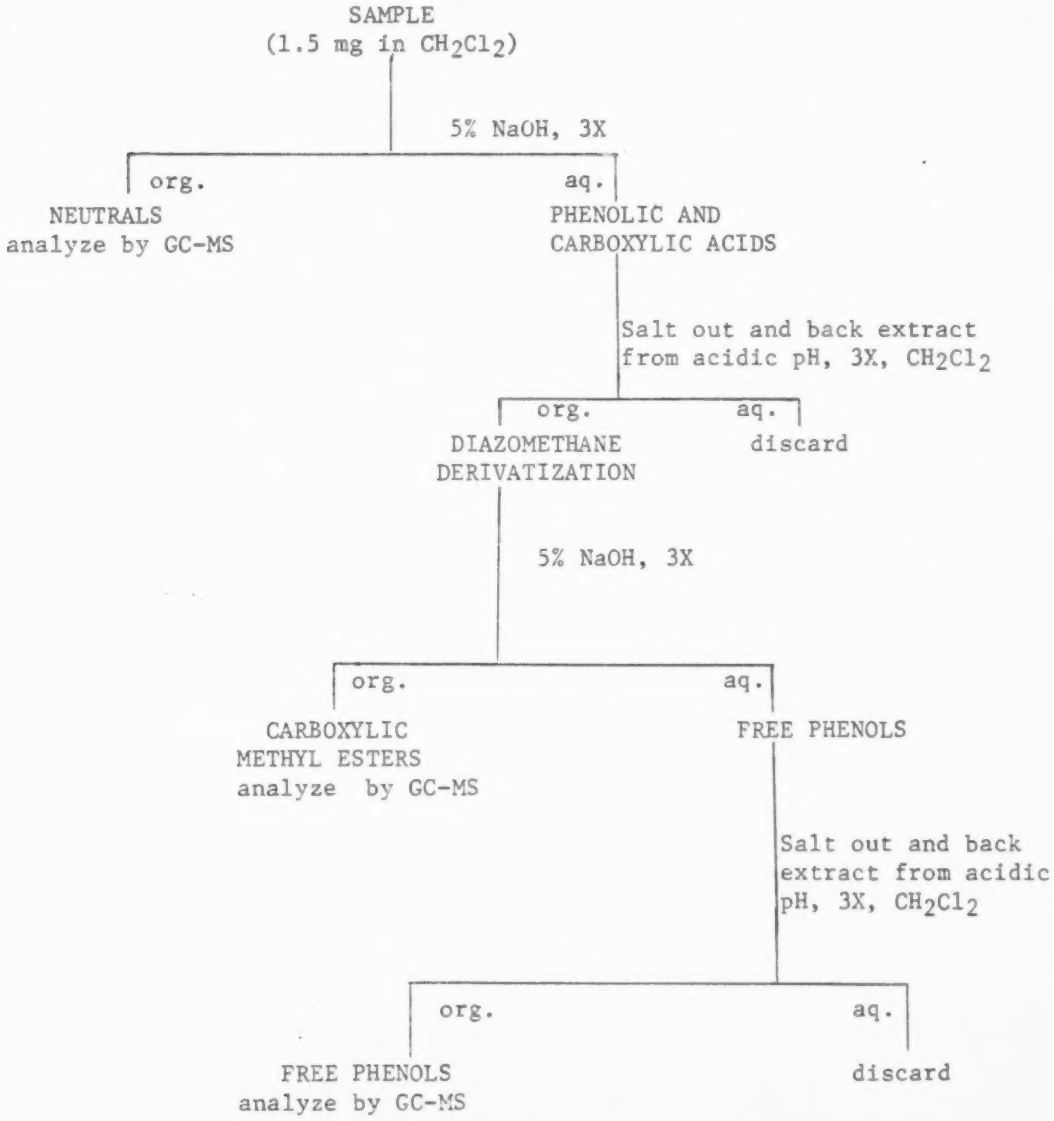
I. Capillary Column Validation.

A newly prepared 30 meter x 0.25 mm ID SE-52 WCOT pyrex column with a film thickness of 0.4μ was evaluated for use in this work. With H_2 carrier at 39.5 cm/sec the column gave an average plate count of 110,000 plates with n-C_{13} and n-C_{14} (SN-43.3). With He carrier (which was used for all analyses) at 22 cm/sec the column gave an average plate count of 94,900 (SN-41.8). Both chromatograms showed an excellent decanol peak (peak height 85% to 90% of the C_{13} peak) with only slight tailing. The Grob test mix indicated the weak acid:base ratio to be nearly unity (phenol and aniline) while the strong acid:base behavior was slightly acidic (2-ethylhexylcarboxylic acid and dicyclohexyl amine). Thus, the column clearly exceeded the specifications promised in our letter of December 14. The superior performance of this column is easily visualized in any of the $(GC)^2$-FID chromatograms accompanying this report.

II. Foam Extract Fractionation.

A sufficient quantity of the March 5, 1979 collapsed foam sample to provide 1.5 mg of material, residue weight basis, was fractionated according to the scheme proposed in our letter of December 14, reproduced in Table 1. A parallel, simultaneous blank was also prepared.

TABLE 1. FOAM EXTRACT PARTITIONING SCHEME


SAMPLE
(1.5 mg in CH_2Cl_2)
5% NaOH, 3X
org.
aq.
NEUTRALS
analyze by GC-MS
PHENOLIC AND
CARBOXYLIC ACIDS
Salt out and back extract
from acidic pH, 3X, CH_2Cl_2
org.
aq.
DIAZOMETHANE
DERIVATIZATION
discard
5% NaOH, 3X
org.
aq.
CARBOXYLIC
METHYL ESTERS
analyze by GC-MS
FREE PHENOLS
Salt out and back
extract from acidic
pH, 3X, CH_2Cl_2
org.
aq.
FREE PHENOLS
analyze by GC-MS
discard

III. $(GC)^2$-FID and Residue Weight Analysis of the Fractionated March 5, 1979 Sample.

Residue weight analysis of the March 5, 1979 fractions and blanks gave results as shown in Table 2.

TABLE 2. RESIDUE WEIGHT ANALYSIS

	Calculated residue weights (mg)			
	Sample	Blank	Net	% of Total
Neutral fraction	1.28	0.014	1.27	91
Carboxylic methyl ester	0.14	0.009	0.13	9
Free phenols	0.018	0.020	0	0
Total			1.40	

These results are somewhat surprising since our prediction from our $(GC)^2$-MS analysis of the methylated unpartitioned March 5, 1979 sample (report, October 26, 1979) was that carboxylic acids were a major component of the sample. Table 2 shows that only 9% of the sample was removable as carboxylic acids. Even more surprising is the lack of the "free phenol" material which we previously hypothesized was present as lignin breakdown products and constituted a major portion of the sample. A possible explanation for the free phenol results is that these materials are not well recovered into aqueous base from methylene chloride solution and have remained with the neutral fraction. Figures 1, 3 and 5 show the $(GC)^2$-FID chromatograms of the neutral, methylated carboxylic acid and free phenol fractions, respectively, while the corresponding process blanks are shown in Figures 2, 4 and 6. These sample and blank chromatograms are clearly consistent with the data of Table 2.

IV. $(GC)^2$-MS Analysis of the March 5, 1979 Sample

Based on the $(GC)^2$-FID chromatograms (Figures 1 through 6), it was decided that a cost-effective approach required the analysis of only three samples by $(GC)^2$-MS: the neutral components, the carboxylic acid methyl esters, and the carboxylic acid methyl ester blank. The labeled reconstructed gas chromatograms of the mass spectral data for these three samples are shown in Figures 7, 8, and 9 respectively. Our processing of the $(GC)^2$-MS data has been limited up to this point pending further instructions from E. C. Jordan Co. Inc. Our present limited analysis includes the following.

Analysis of the Neutral Components. Mass spectra of the 36 largest GC peaks have been corrected for background, plotted and matched against the 31,300 NIH/EPA/NSRDS mass spectral library using Finnigan INCOS software. The results are indicated on the chromatogram of Figure 7. The largest component is well-identified as the aldehyde analogue of dehydroabietic acid (peak 24), while the aldehyde analogue of abietic acid (peak 23) appears as a partially resolved component just prior to it at approximately 30% relative concentration. Unfortunately, the two components next highest in concentration (peak #7 and #30) remain unidentified at this time. Their mass spectra appear as Figures 10 and 11, respectively. Neither of these spectra show evidence of a molecular ion. Of the limited number of GC peaks (36) which have been inspected, 9 appear to be resin acid based neutrals with partially reduced phenanthrene or naphthalene nucleii (peaks 4, 5, 9, 18, 19, 20, 23, 24 and 26); 6 appear to be fatty alcohols, both saturated and unsaturated (peaks 2, 17, 32, 35, 37 and 39); 4 peaks are probably phenolic or phenoxy lignin breakdown products (peaks 8, 11, 22 and possibly 31); 9 peaks remain unidentified (peaks 3, 6, 7, 27, 28, 30, 34, 36 and 38); two peaks are apparently unsaturated hydrocarbons (peaks 25 and 33); and 3 peaks are possible artifacts (phthalates) of sampling prior to our fractionation since they do not appear in our blank (peaks 13, 14-16, and 29). Two peaks (#12 and 31) are fatty acids due to incomplete extraction.

The most immediate conclusion to be drawn from Figure 7 is that 80 to 90% of the GC analyzable neutral components are present as a plethora of species at relatively low concentration (1% to 5% of the most concentrated component). Computer matching and manual interpretation of the mass spectra of all the peaks of Figure 7 would yield a more complete picture of the types and relative amounts of the components of this very complex mixture. However, the high extent of coelution suggests that extensive mass spectral data work-up will be less than optimally effective. It is clearly evident from the chromatogram that the chromatographic performance is superb, and therefore, little new information could be gained from further chromatographic optimization. A more logical choice would be fractionation of the neutrals components on silica gel to yield three to five polarity groups. We are routinely performing this type of fractionation in other programs on a micro scale (silica gel column with void volume = 1.75 ml), and can easily produce a set of fractionated neutral components for analysis by (GC)^2-FID or, if judged useful, by (GC)^2-MS.

Analysis of the Methylated Carboxylic Acids. The reconstructed gas chromatograms of the (GC)^2-MS analysis of the extracted, methylated acid sample and the parallel blank sample are shown in Figure 8 and 9, respectively. These chromatograms have been labeled to indicate the identification results which are currently available. Our initial data interpretation effort has been limited to the following preliminary effort:

- Using the mass spectral and (GC)^2 retention time data from the analysis of fatty and resin acid standards (see section VI, below) the (GC)^2-MS data was specifically searched for these compounds. These extracted ion current profiles (EICP) use ions which are relatively specific for the compounds in question.

- The mass spectra of the major peaks which were not identified by the EICP computerized search of the (GC)^2-MS data were matched against the 31,300 spectrum NIH/EPA/NSRDS library. The matching results were inspected and a brief attempt at manual interpretation of unidentified spectra was made.

- Computerized single and multiple m/e EICP chromatograms were produced using ions which indicate the presence of specific functional groups or classes of compounds.

Information generated from these three data processing steps has yielded the identification results which appear on the chromatogram of Figure 8.

Dichlorodehydroabietic acid, one isomer of chlorodehydroabietic acid, tetrachloroguiacol, trichloroguiacol and dehydroabietic acid (all as the methyl derviatives) have been found in very low concentration. Abietic acid, pimaric (or isopimaric) acid and a number of other unidentified but apparently phenanthrene nucleus resin acid related components were found in somewhat higher concentration. The epxected range, from C-6 to C-26, of fatty acids (as the methyl esters) have been detected. However, the same fatty acids are observed in the blank as well, and the similarity of relative amounts of laurate, myristate, palmitate, and stearate, make it impossible to definitively say that these materials were present in the March 5, 1979 sample. Comparing peak height ratios of these fatty acid methyl esters to the hexaethylbenzene internal standard, it seems clear that there is significantly more oleic, C-6 through C-10 and C-20 through C-26 fatty acid in the March 5, 1979 sample than there is in the blank. For comparison, the m/e 74 and 87 EICP chromatograms of sample and blank are shown in Figures 12 and 13, respectively. The m/e 59 EICP chromatogram, Figure 14, indicates a preponderance of carboxylic acid, methyl ester species, as expected, and clearly highlights the resin acid region from spectrum 1100 to about spectrum 1500. Figures 15, 16, 17 and 18 show EICP chromatograms which indicated the presence of chloro and dichloro methyl abietate and trichloro and tetrachloro guiacol methyl ether, respectively, as extremely low level sample components. In each case, the background subtracted spectrum was inspected to verify the identification.

To summarize, the fraction of the March 5, 1979 sample which can be partitioned into aqueous base consists principally of resin acid related carboxylic acids. The expected major constituents, abietic, dehydroabietic, pimaric or isopimaric, chlorinated abietics, and chlorinated guiacols have been definitively identified. There are, however, many compounds whose structures cannot be specified at this time but whose mass spectra clearly indicate that they are resin acid related compounds.

V. $(GC)^2$-FID Chromatograms and Residue Weight Determination of the "Dam No. 2" and "Dam No. 12" Samples.

The "Dam No. 2" sample was a solution of about 550 µl volume which contained 3.03 mg of material on a residue weight basis. The corresponding values for the "Dam No. 12" sample were about 1300 µl and 9.8 mg, respectively. The $(GC)^2$-FID chromatograms for these samples are shown in Figure 19 (Dam No. 2) and 20 (Dam No. 12). The chromatograms for these two samples are quite similar to each other and, not surprisingly, appreciably different from the fractions of the March 5, 1979 sample. The main feature to note in comparing the "Dam No. 2" sample with the "Dam No. 12" sample is that the latter is the large "hump" of unresolved, late eluting material. On a ng/µl basis, the "Dam No. 12" sample has 50% more material than the "Dam No. 2" sample, and this excess material appears to be principally responsible for the "hump" in Figure 20. It is clear from the $(GC)^2$-FID chromatograms that fractionation on silica gel would be necessary for the maximum degree of chemical characterization by $(GC)^2$-MS.

VI. $(GC)^2$-MS Analysis of Resin and Fatty Acid Standards.

Table 3 displays the fourteen resin and fatty acids which are know contaminants of pulping mill effluent and which were available in-house at the time of this work. Also shown are the relative retention times (RRT) of each material on the 30 meter SE-52 glass capillary column which was used for this work. The data from this analysis was used to specifically search the $(GC)^2$-MS data for the carboxylic acid fraction of the March 5, 1980 sample. We have now found a source of a number of resin acids and other compounds related to pulping effluents, and we are in the process of obtaining the following compounds:

Neoabietic acid
Levopimaric acid
Palustric acid
Sandaracopimaric acid
Various chlorinated catechols and guiacols.

These compounds will provide the data base for further identifications of compounds in acid fractions of samples.

We apologize for the delay in getting this information to you -- we trust it will be useful.

Please call us if you have any questions.

Very truly yours,

Samuel V Lucas

Samuel V. Lucas
Research Scientist
Environmental and Health Chemistry

R.E. Heffelfinger

R. E. Heffelfinger
Projects Manager
Analytical Chemistry

SVL/REH:lj

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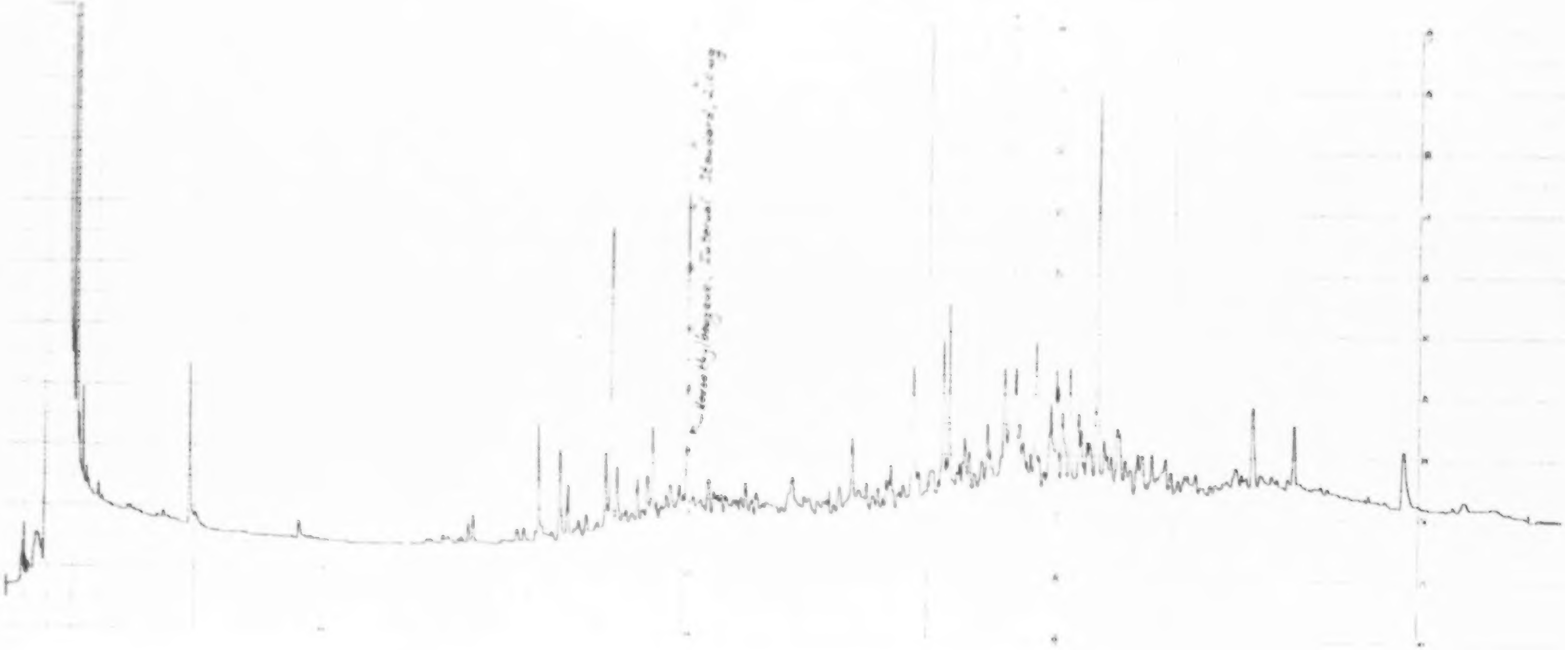
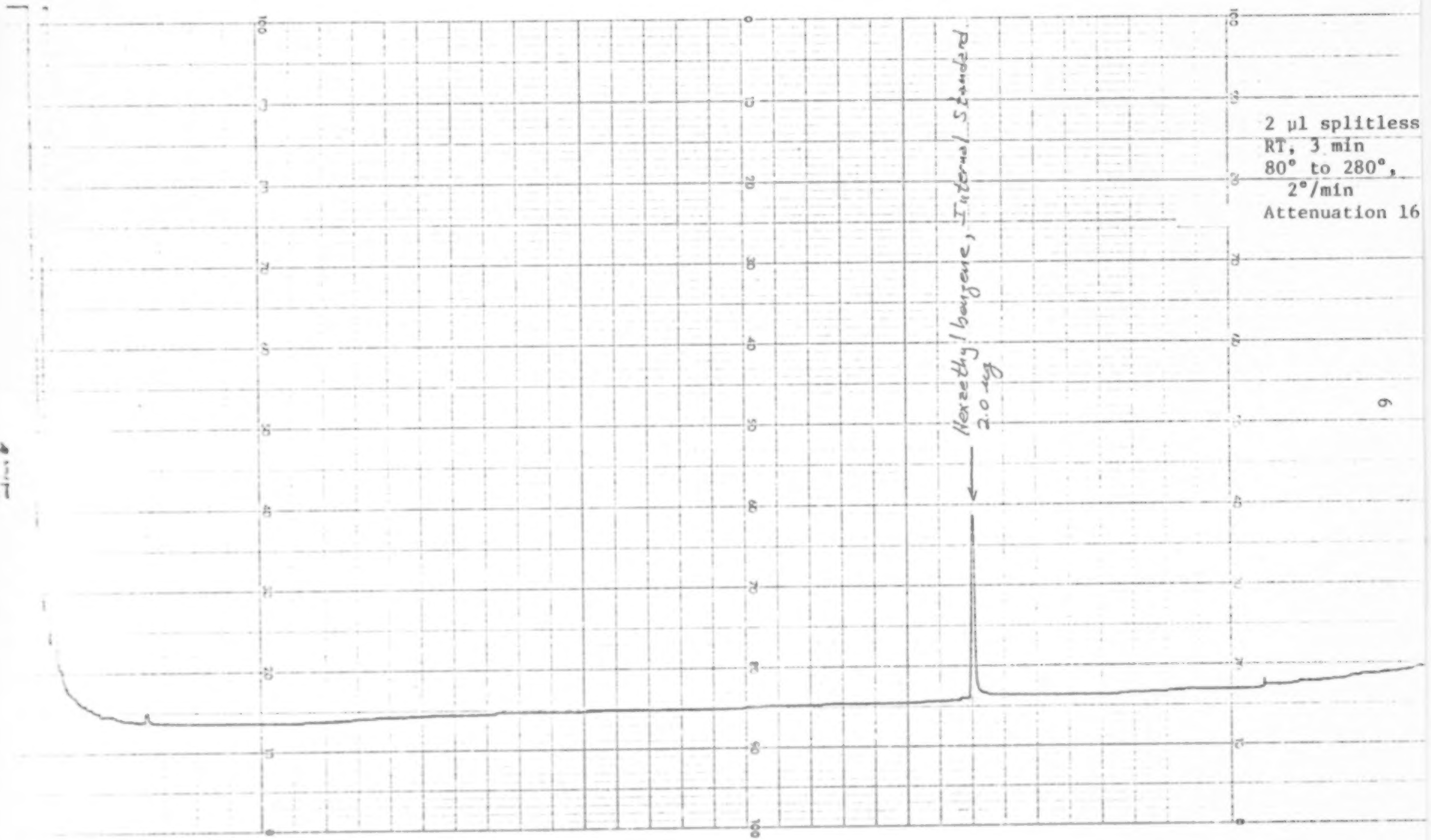


FIGURE 1. $(GC)^2$-FID CHROMATOGRAM OF THE NEUTRALS FRACTIONATED FROM THE MARCH 5, 1979 SAMPLE.



2 µl splitless
RT, 3 min
80° to 280°,
2°/min
Attenuation 16

Hexaethylbenzene, Internal Standard
2.0 ng

FIGURE 2. $(GC)^2$-FID CHROMATOGRAM OF THE BLANK NEUTRALS FRACTION CORRESPONDING TO FRACTIONATION OF THE MARCH 5, 1979 SAMPLE

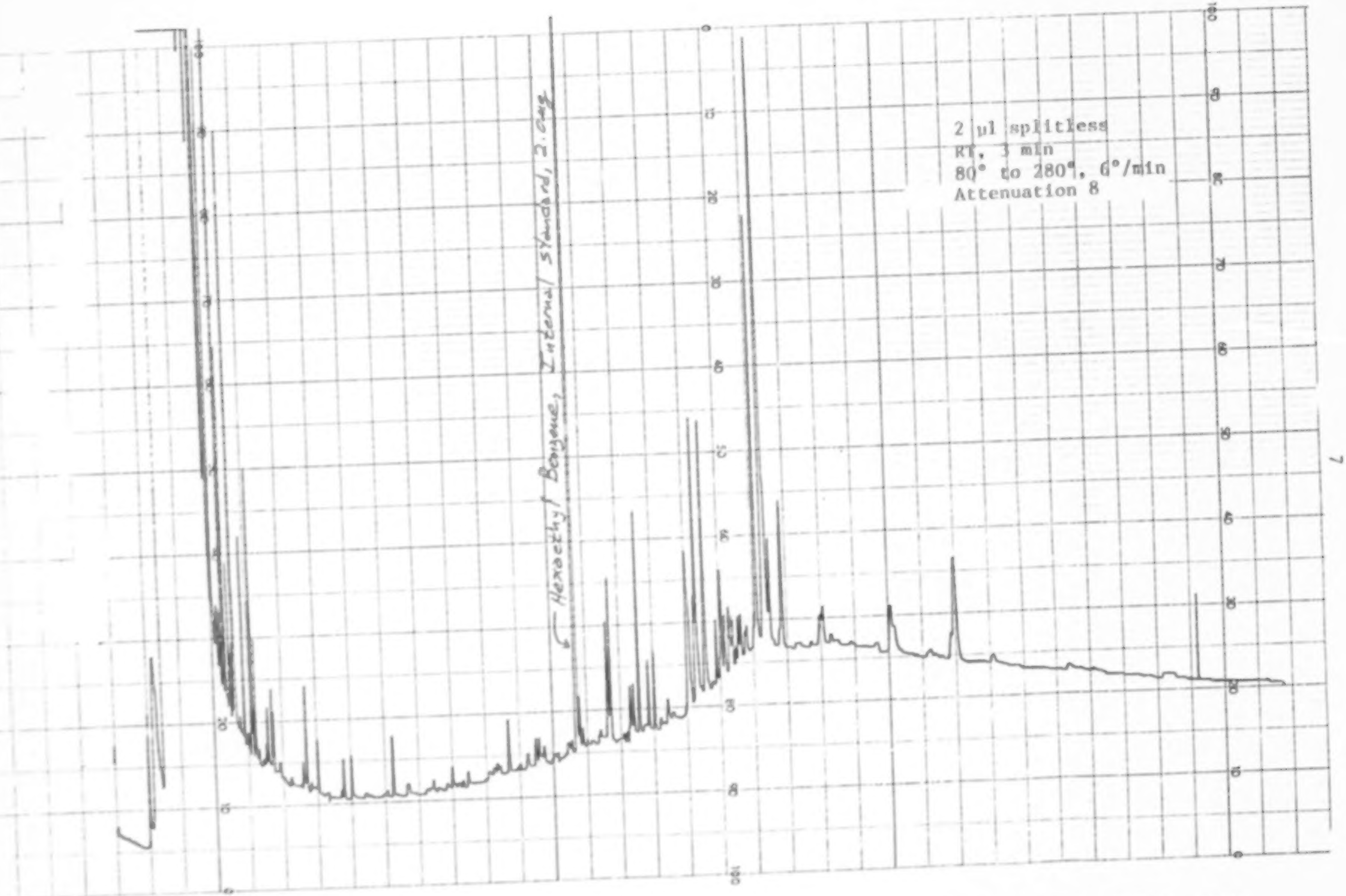


FIGURE 3. (GC)^2-FID CHROMATOGRAM OF THE CH_2N_2 DERIVITIZED STRONG ACID FRACTION OF THE MARCH 5, 1979 SAMPLE.

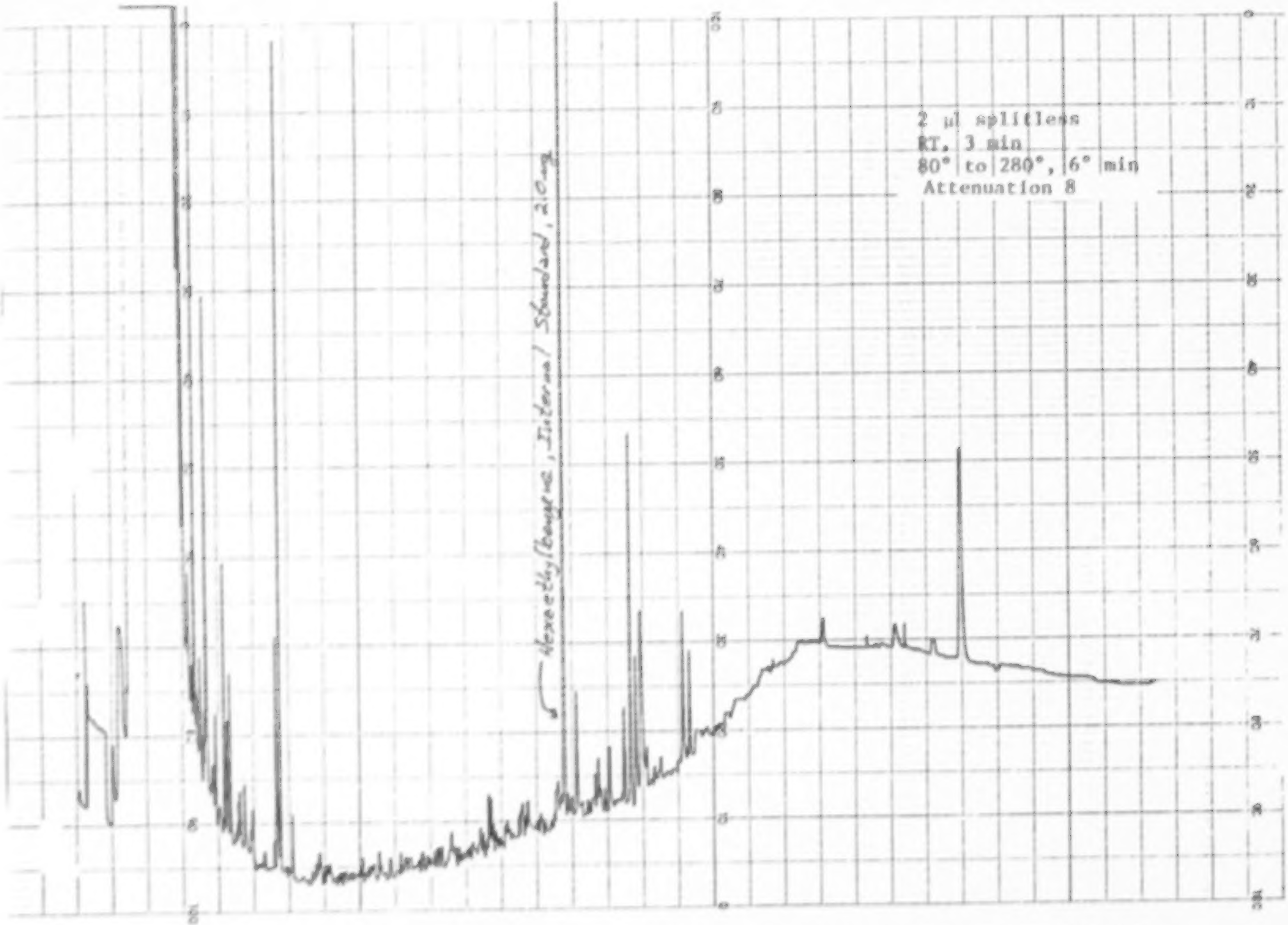
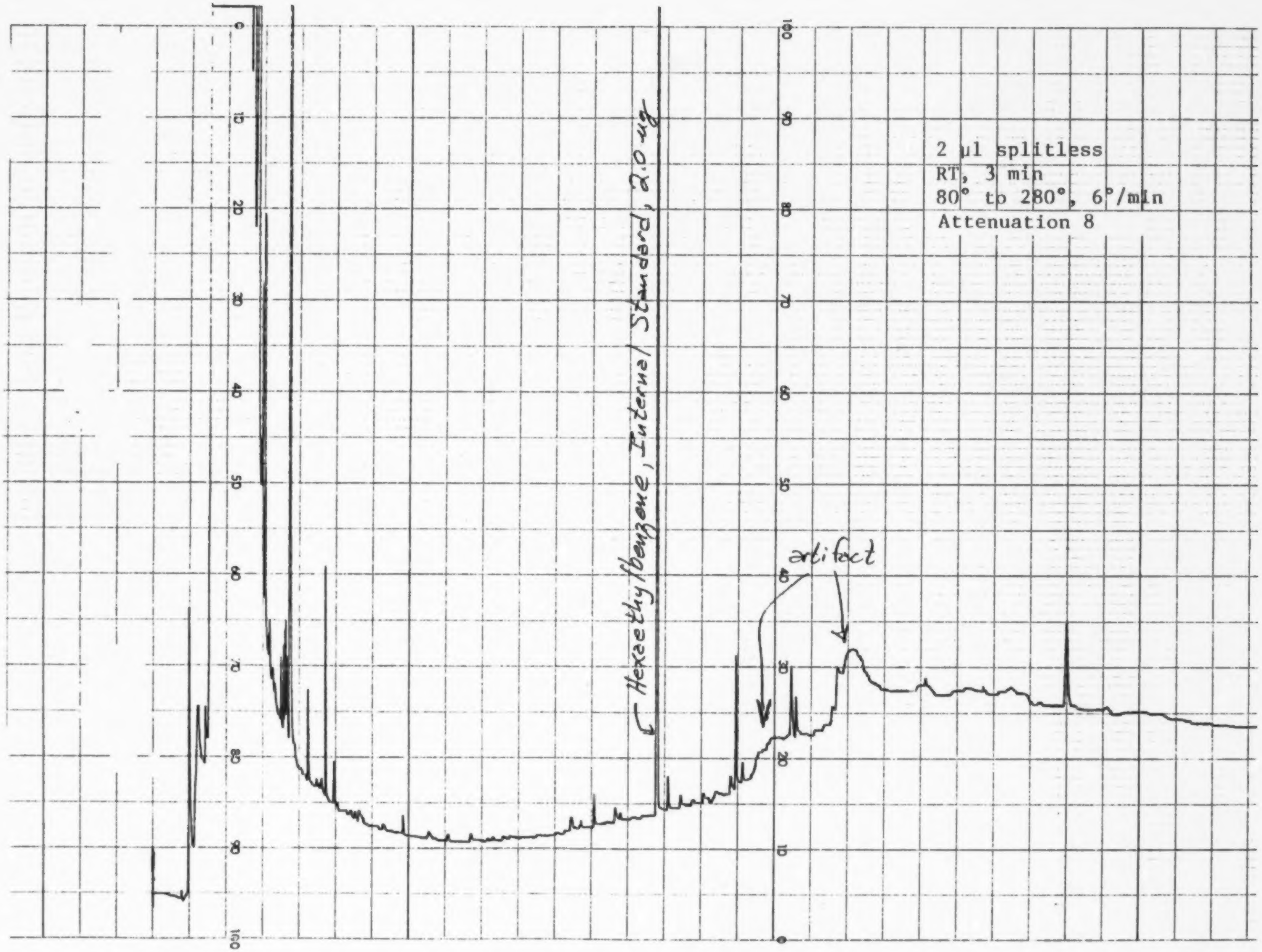


FIGURE 4. (GC)^2- FID CHROMATOGRAM OF THE BLANK CH_2N_2 DERIVITIZED STRONG ACID FRACTION CORRESPONDING TO FRACTIONATION OF THE MARCH 5, 1979 SAMPLE.



2 µl splitless
RT, 3 min
80° to 280°, 6°/min
Attenuation 8

FIGURE 5. $(GC)^2$-FID CHROMATOGRAM OF THE WEAK (UNDERIVITIZED) ACID FRACTION OF THE MARCH 5, 1979 SAMPLE.

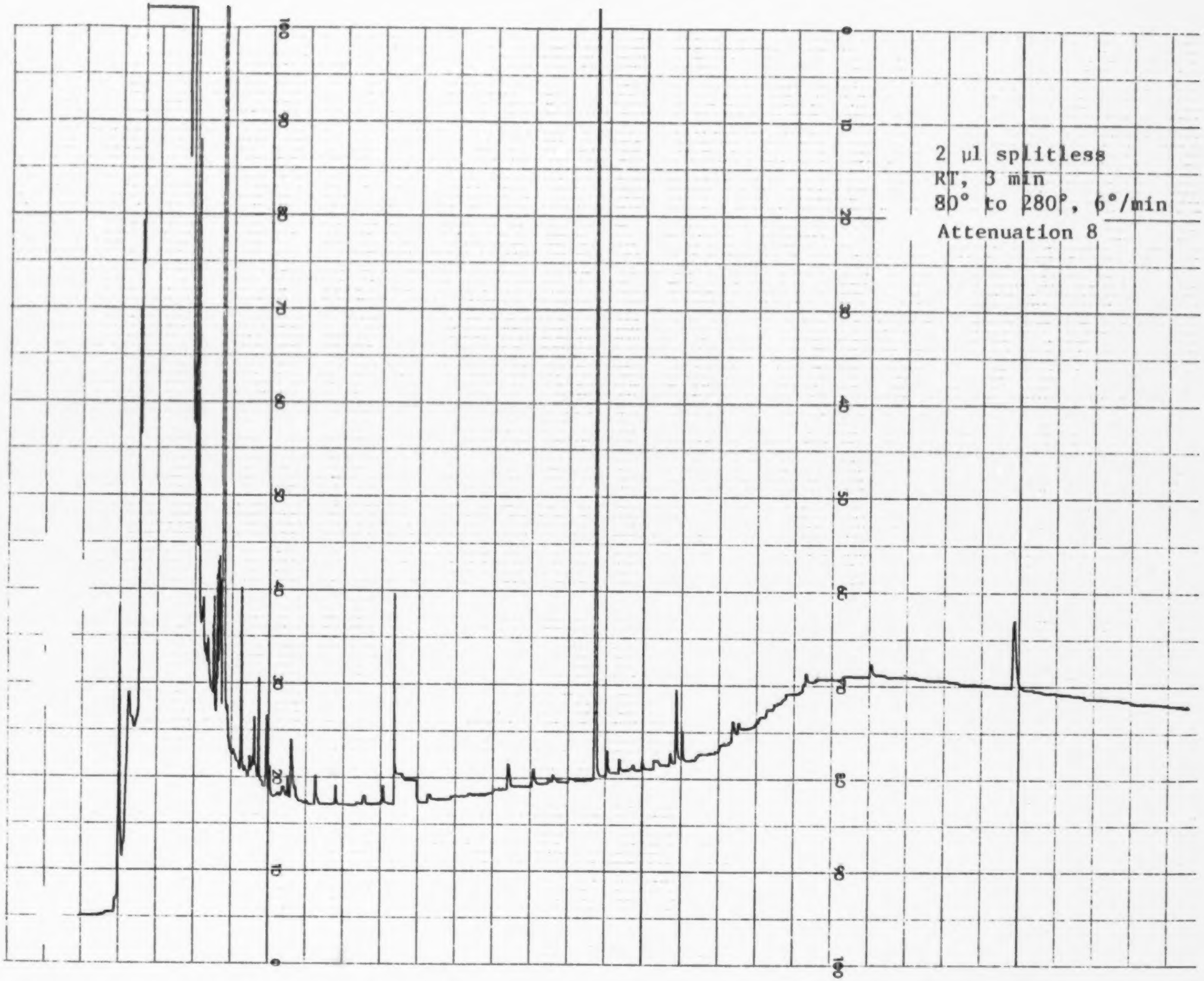


FIGURE 6. (GC)^2-FID CHROMATOGRAM OF THE BLANK WEAK ACID FRACTION CORRESPONDING TO FRACTIONATION OF THE MARCH 5, 1979 SAMPLE.

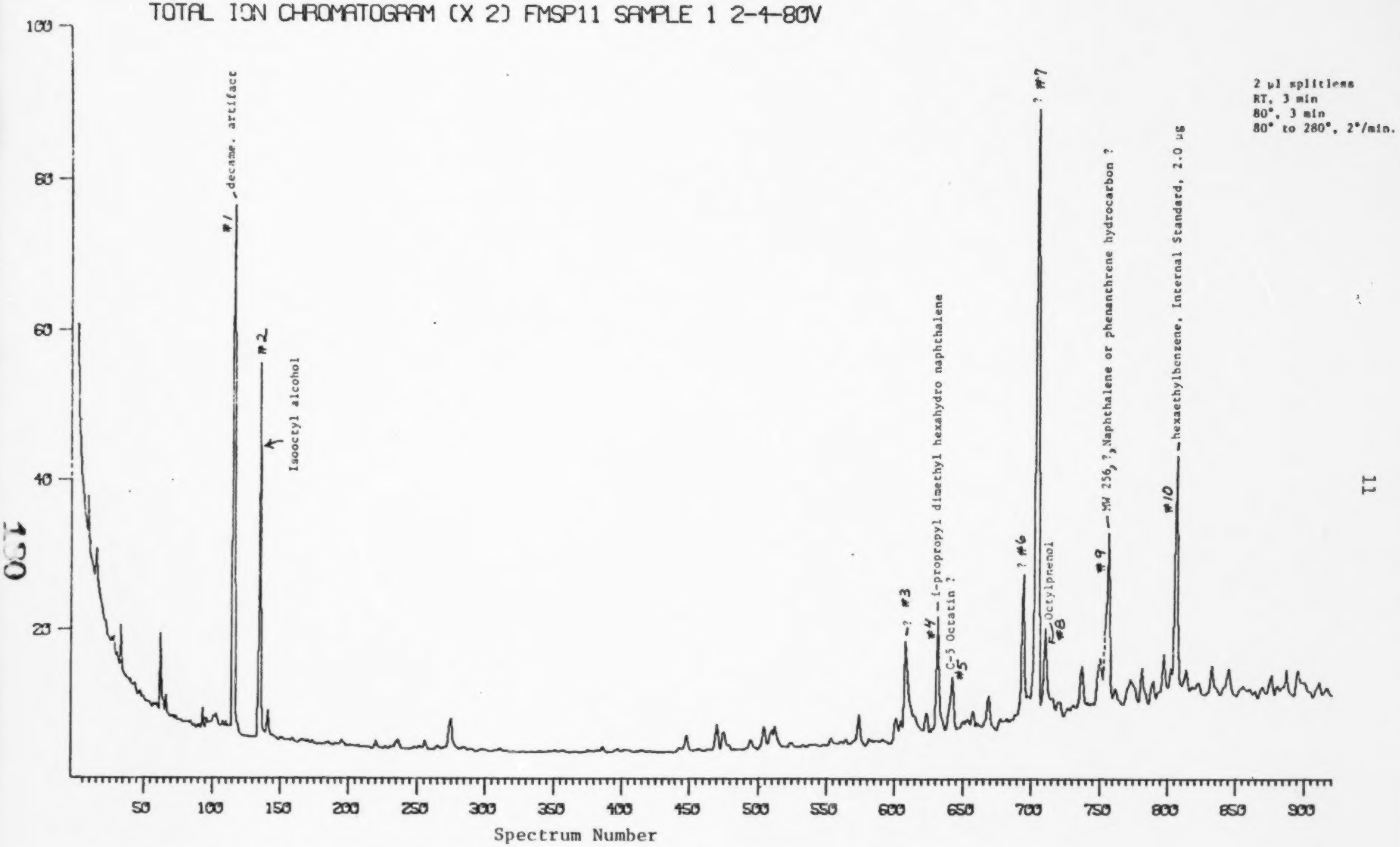


FIGURE 7. (GC)^2-MS CHROMATOGRAM OF THE MARCH 5, 1979 NEUTRALS FRACTION

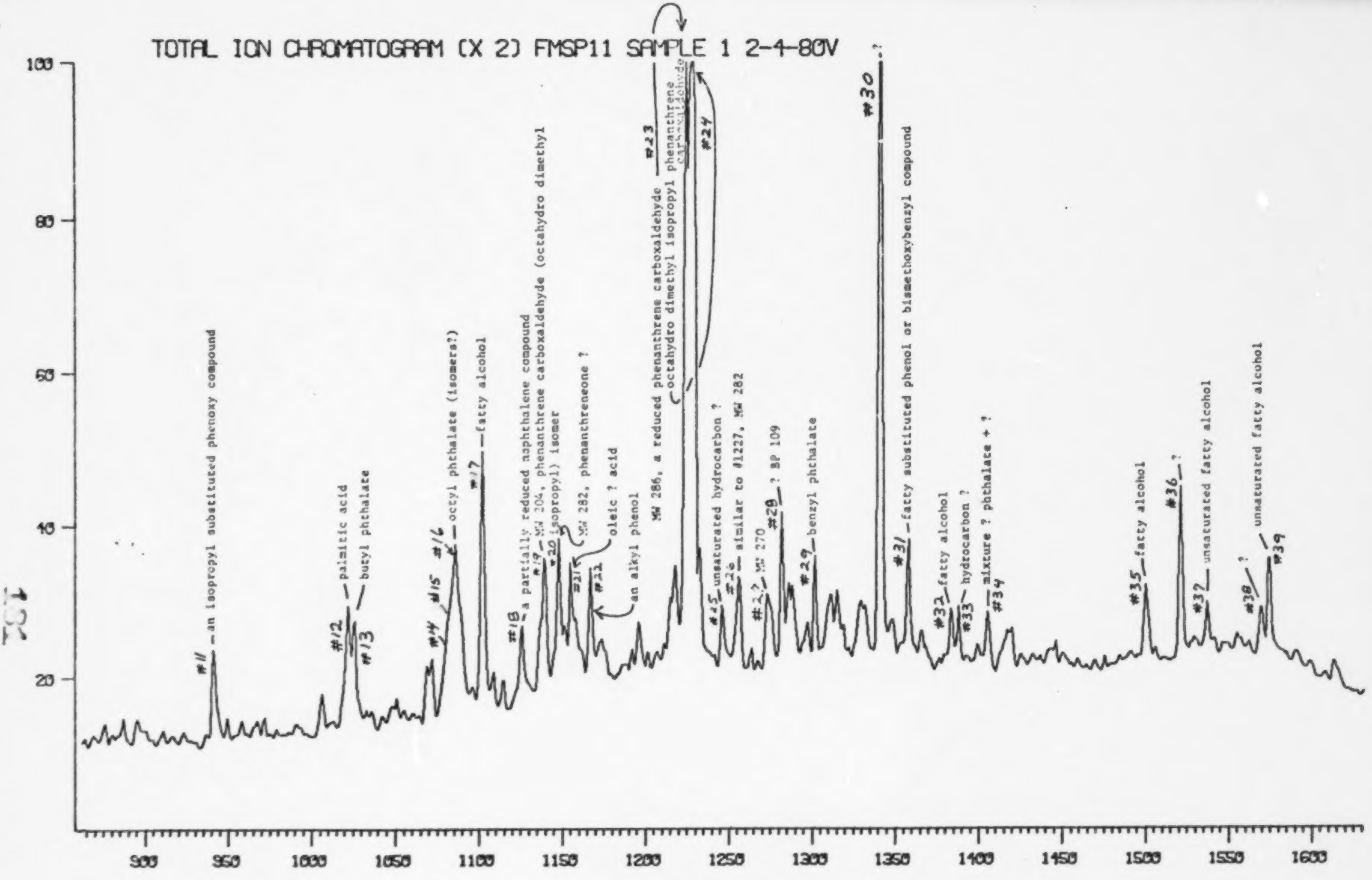


FIGURE 7. (Continued)

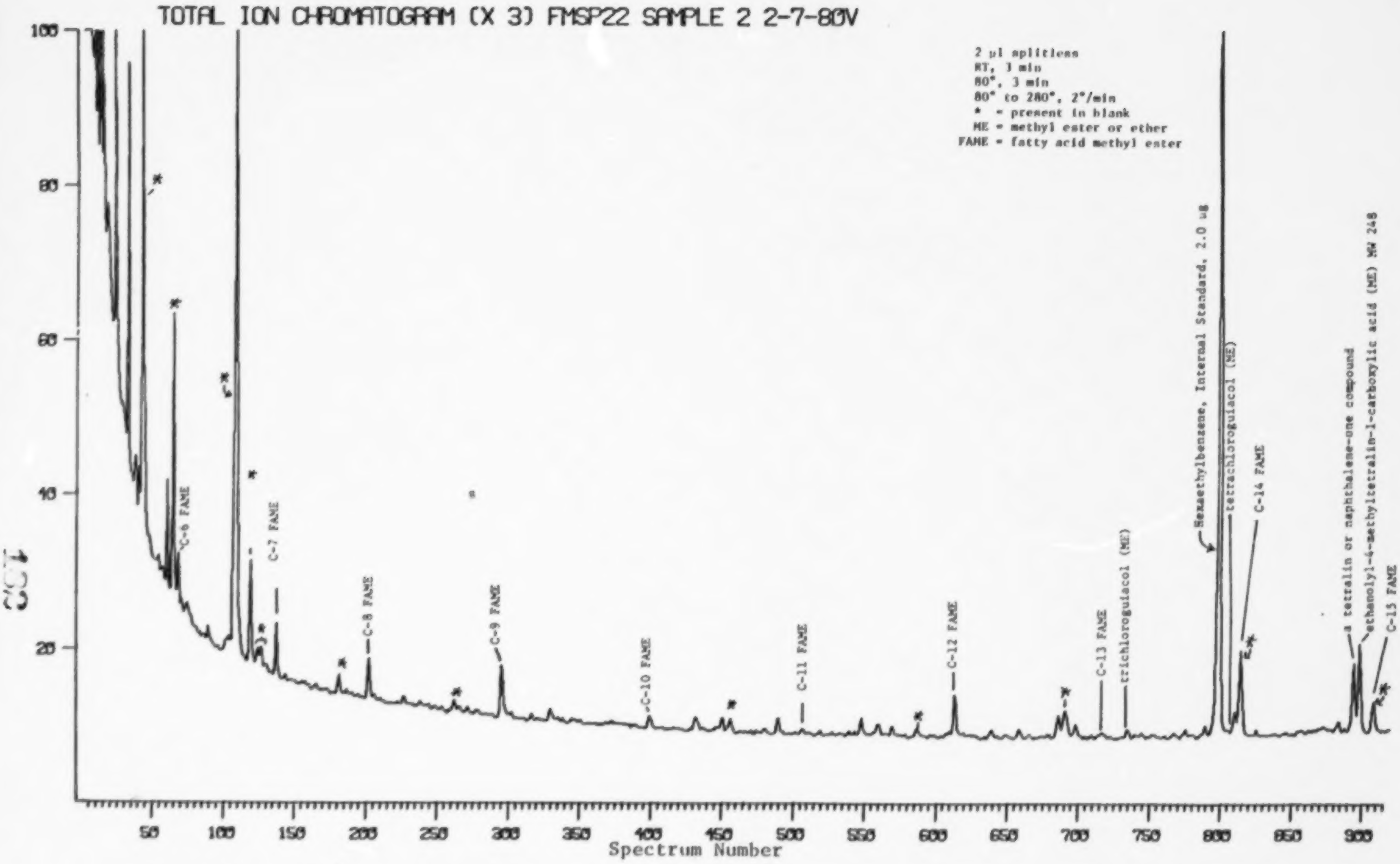


FIGURE 8. $(GC)^2$-MS CHROMATOGRAM OF THE CH_2N_2-DERIVITIZED STRONG ACIDS OF THE MARCH 5, 1979 SAMPLE.

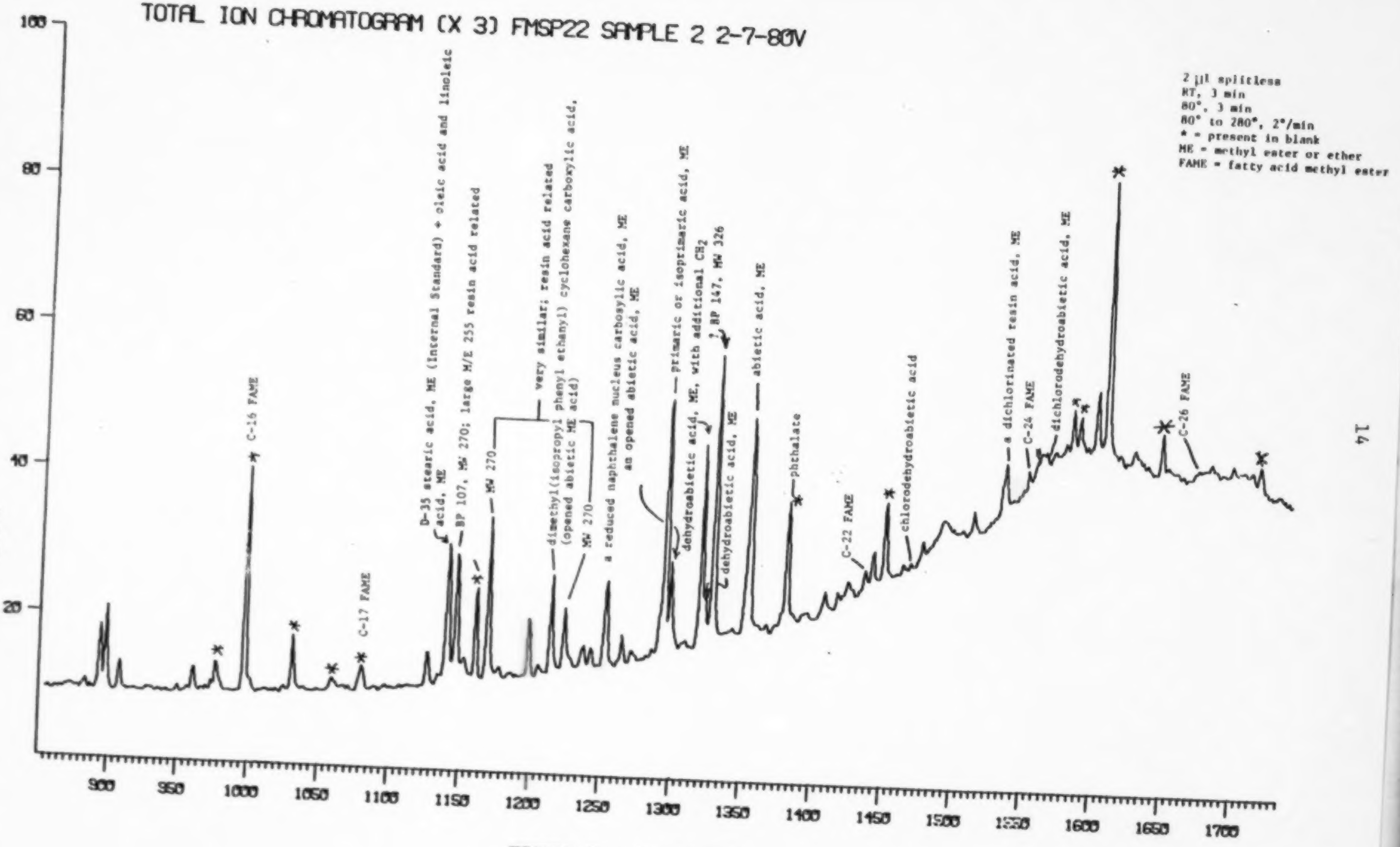
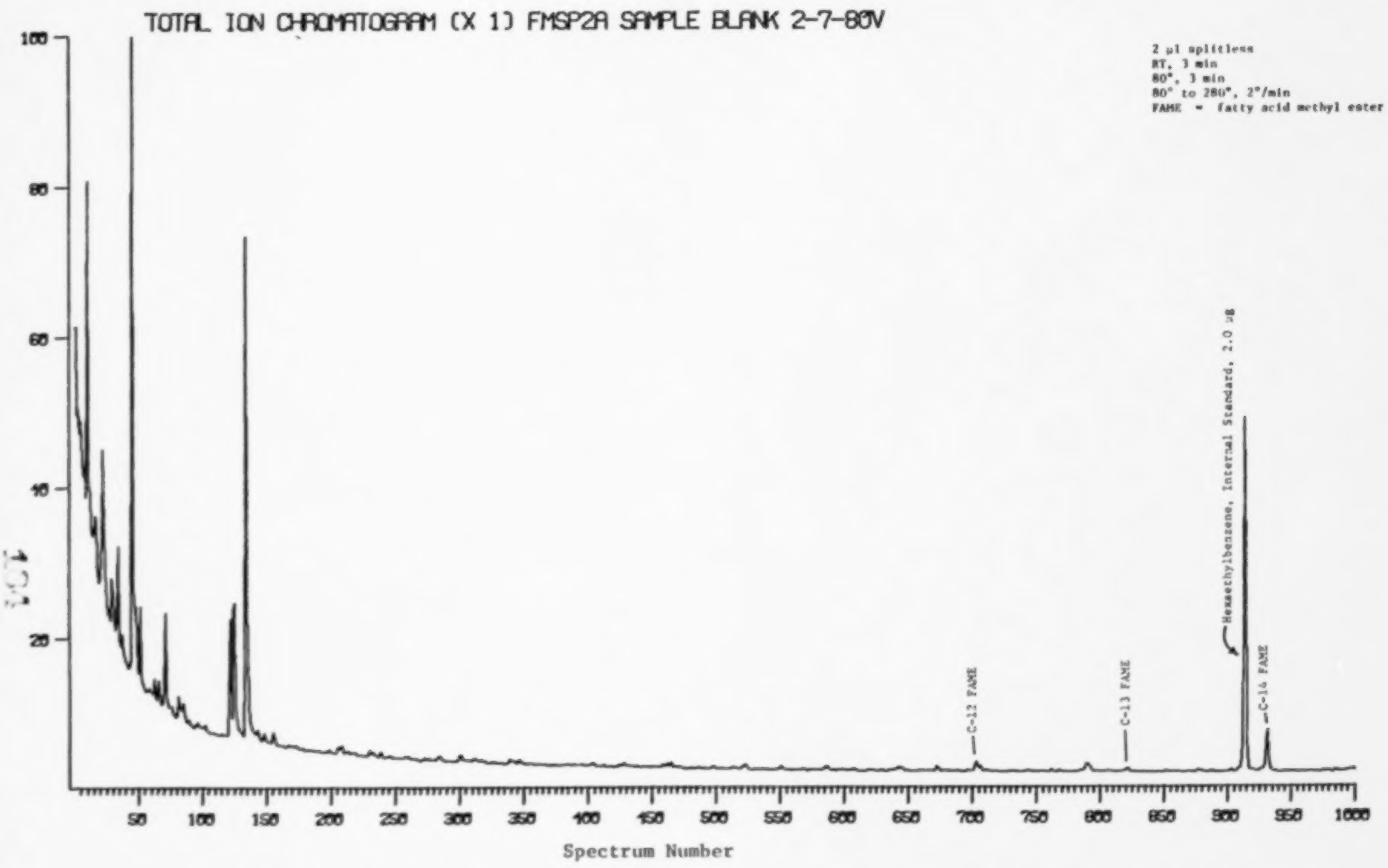


FIGURE 8. (Continued)



2 μl splitless
RT, 3 min
80°, 3 min
80° to 280°, 2°/min
FAME = fatty acid methyl ester

FIGURE 9. (GC)^2-MS CHROMATOGRAM OF THE CH_2N_2-DERIVATIZED STRONG ACIDS OF THE MARCH 5, 1979 SAMPLE.

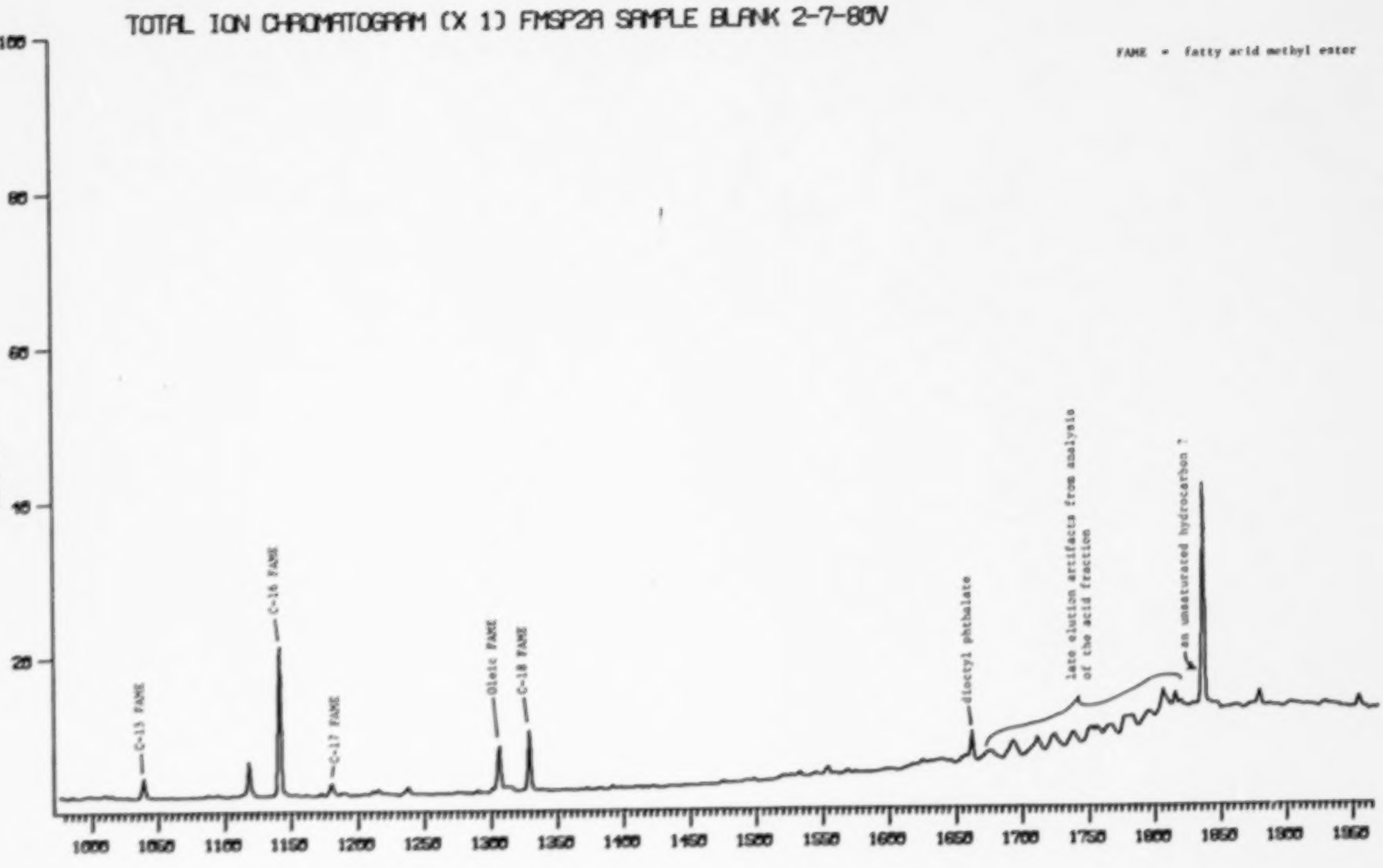


FIGURE 9. (Continued)

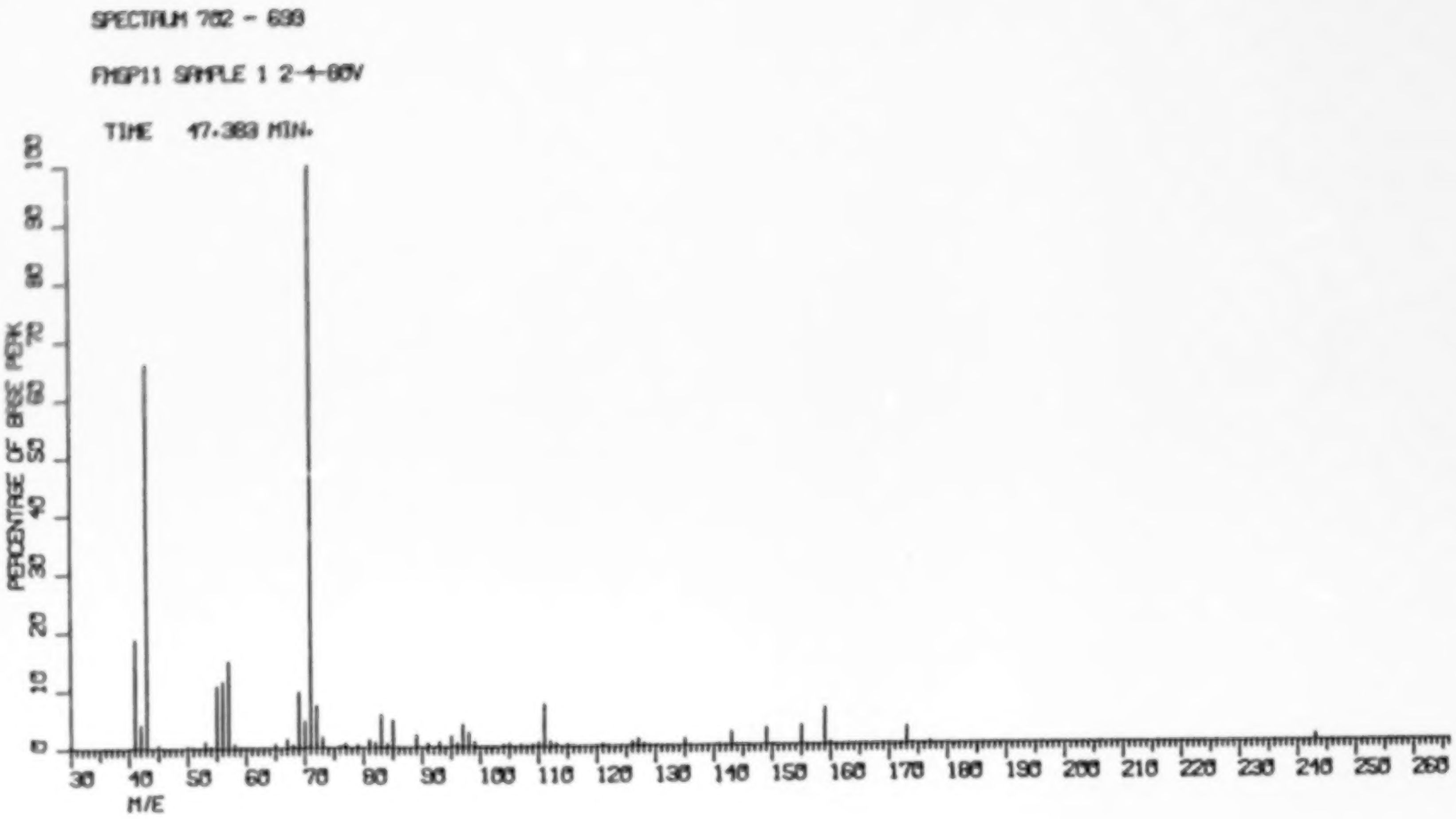


FIGURE 10. MASS SPECTRUM OF A MAJOR UNIDENTIFIED COMPONENT IN THE MARCH 5, 1979 NEUTRAL FRACTION -- PEAK #702 OF FIGURE 7.

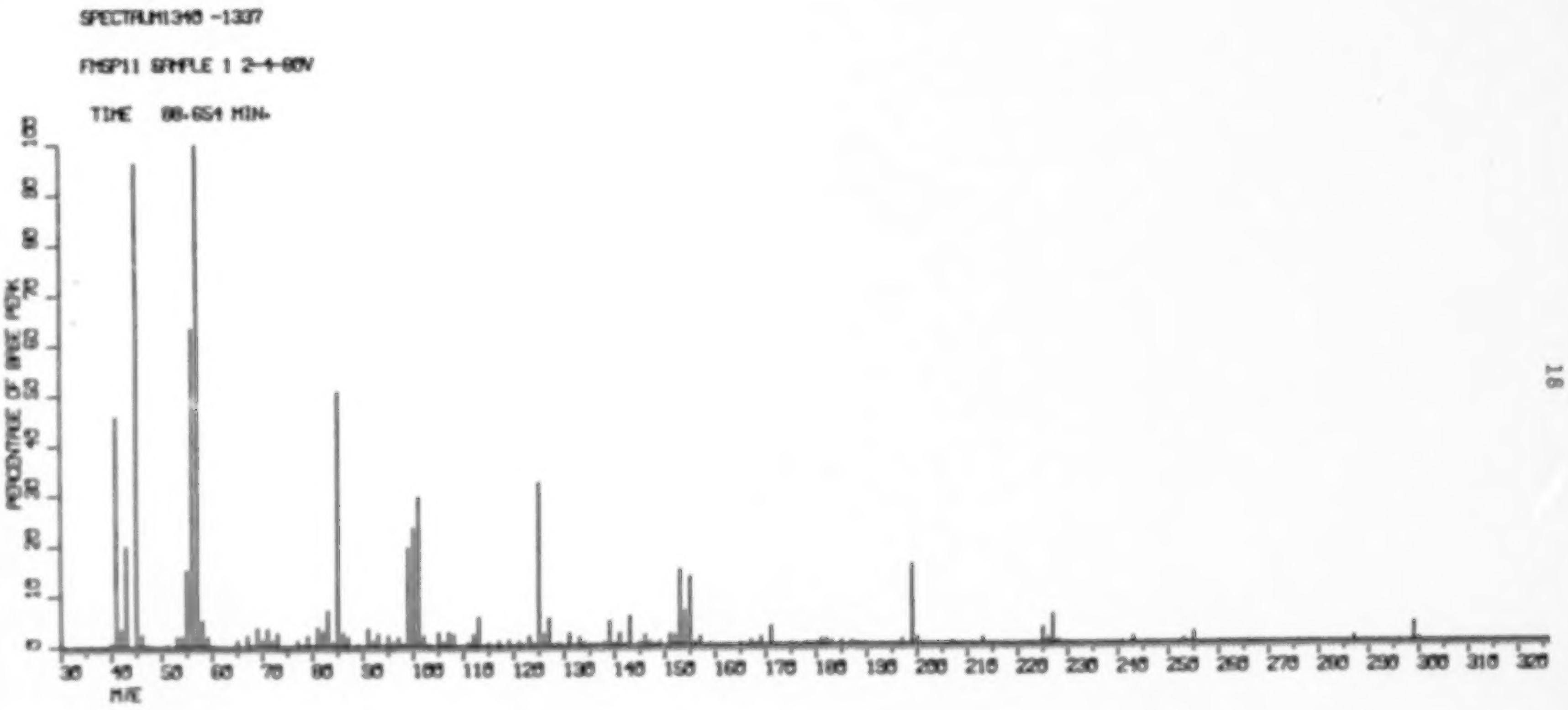


FIGURE 11. MASS SPECTRUM OF A MAJOR UNIDENTIFIED COMPONENT IN THE MARCH 5, 1979 NEUTRAL FRACTION -- PEAK #1340 OF FIGURE 7.

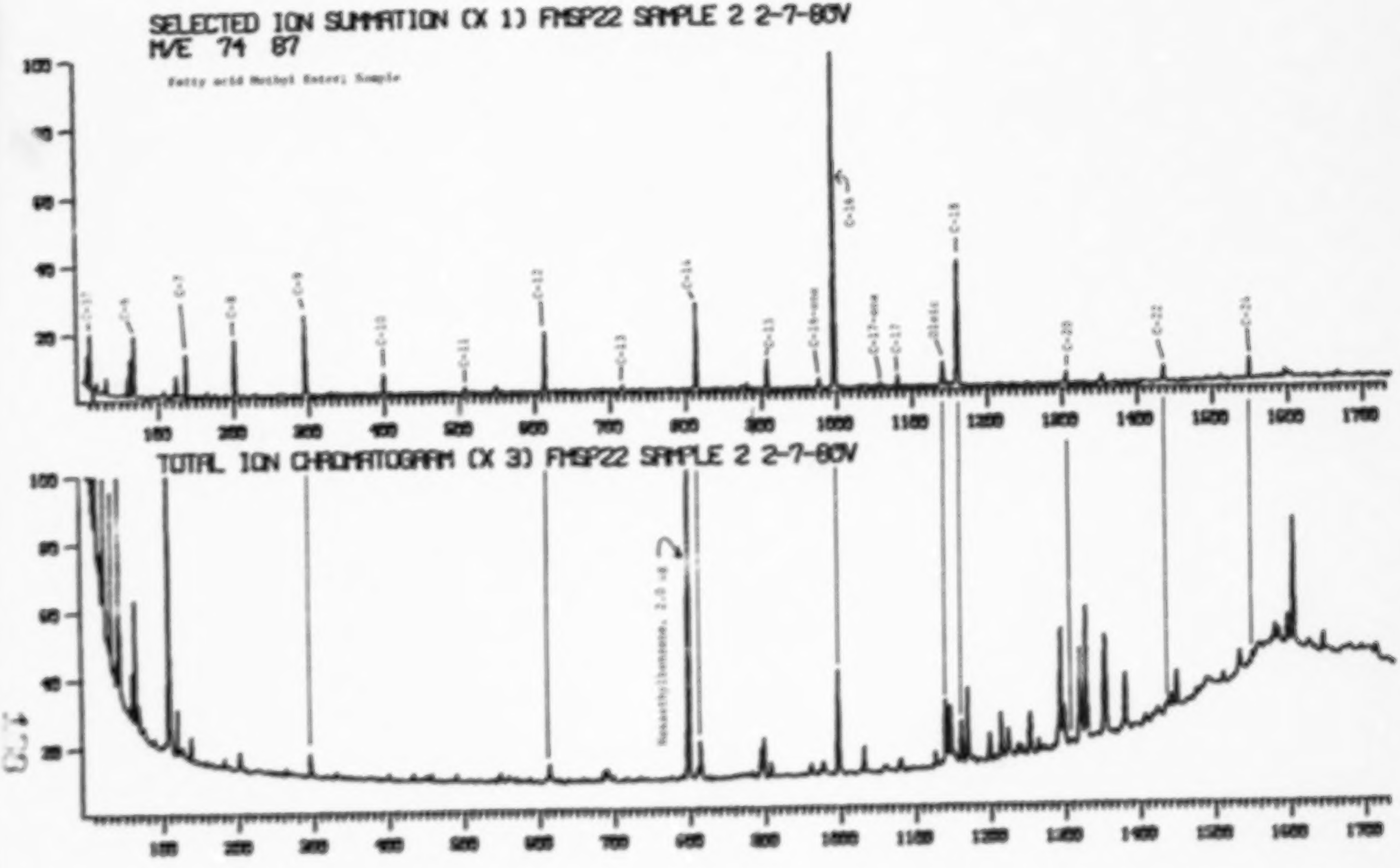


FIGURE 12. EICP CHROMATOGRAM FOR m/e 74 AND 87 -- METHYLATED STRONG ACID FRACTION OF THE MARCH 5, 1979 SAMPLE.

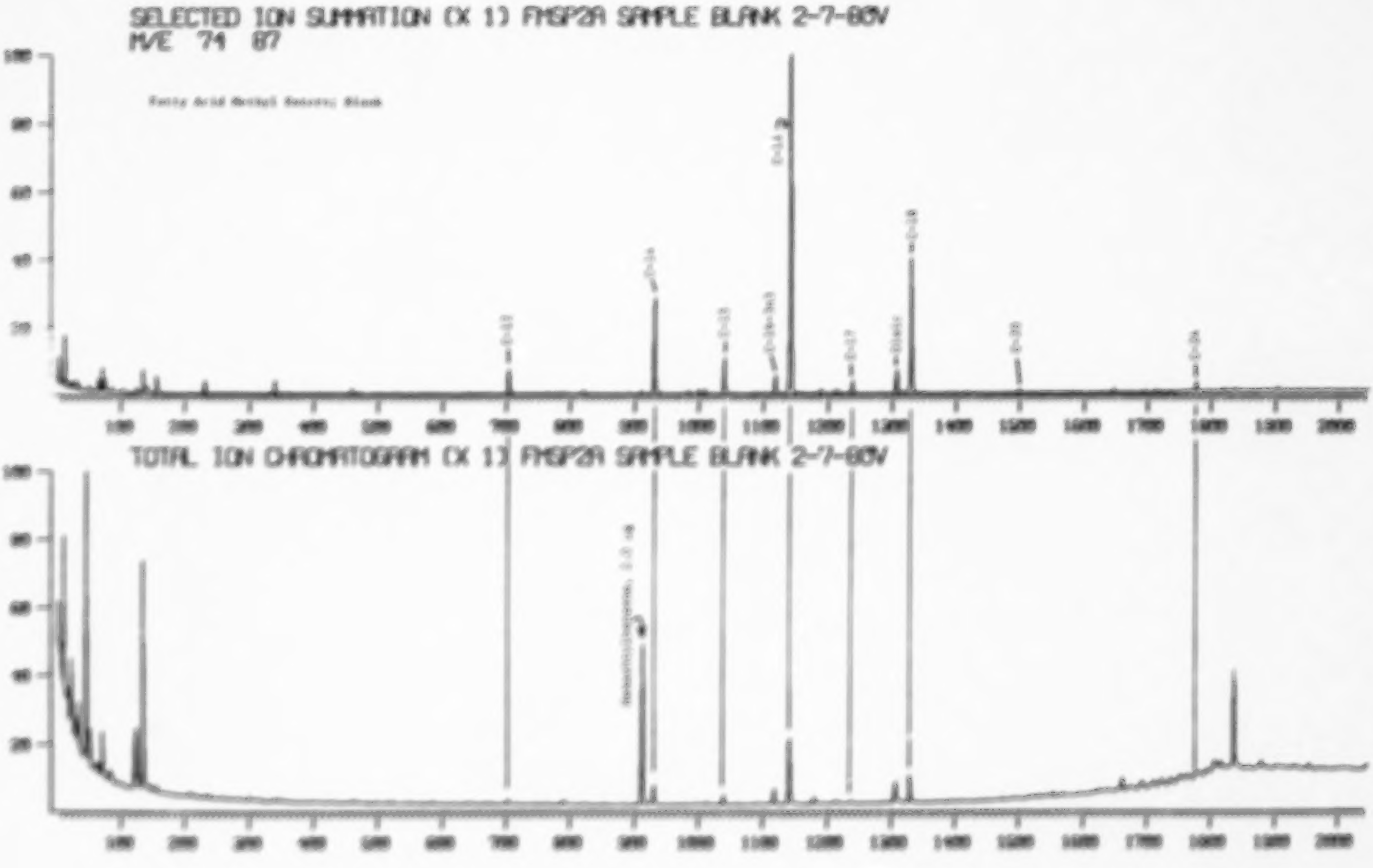


FIGURE 13. EICP CHROMATOGRAM FOR m/e 74 AND 87 -- BLANK CORRESPONDING TO THE METHYLATED STRONG ACID FRACTION OF THE MARCH 5, 1979 SAMPLE.

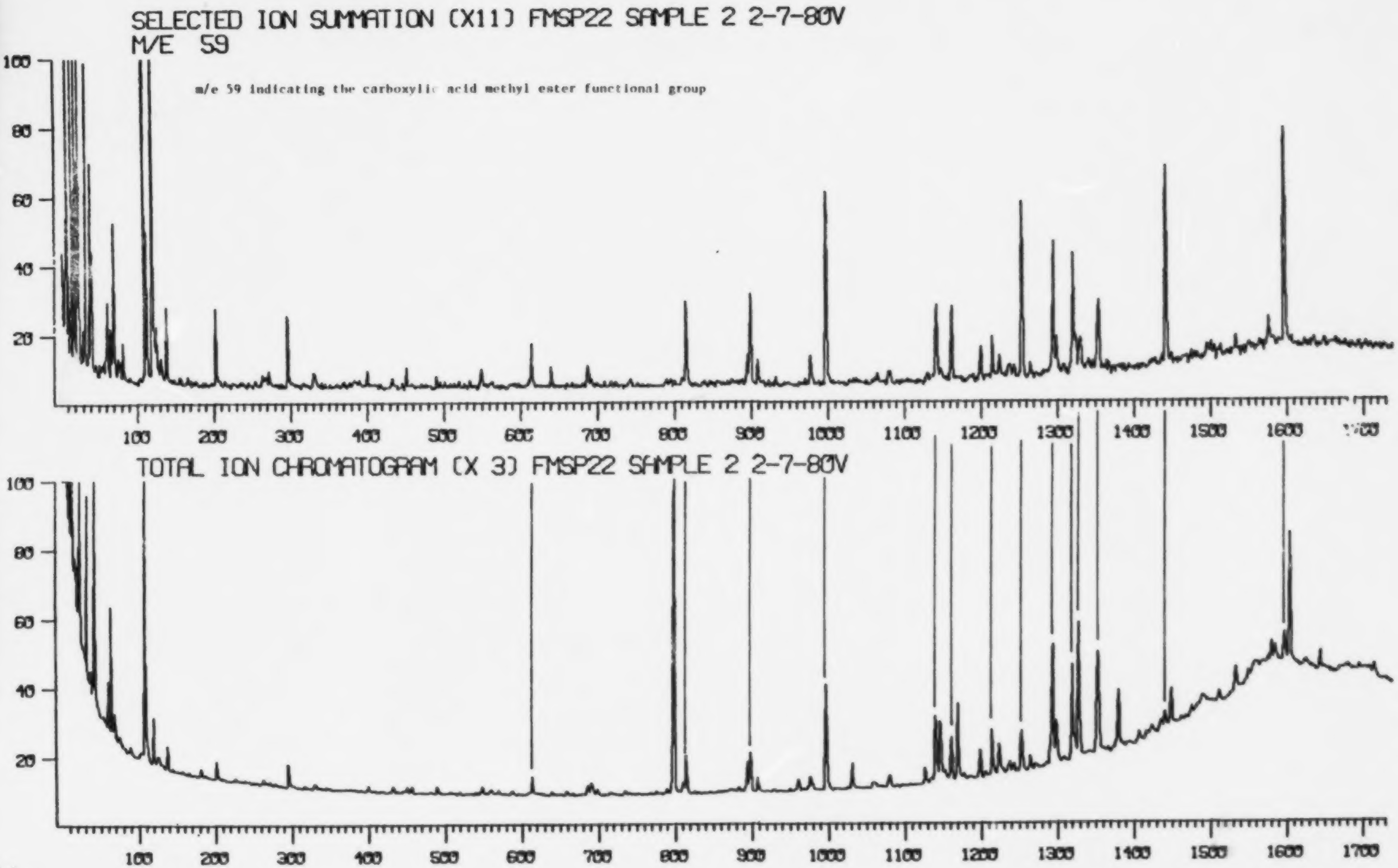


FIGURE 14. EICP CHROMATOGRAM FOR m/e 59 -- METHYLATED STRONG ACID FRACTION OF THE MARCH 5, 1979 SAMPLE.

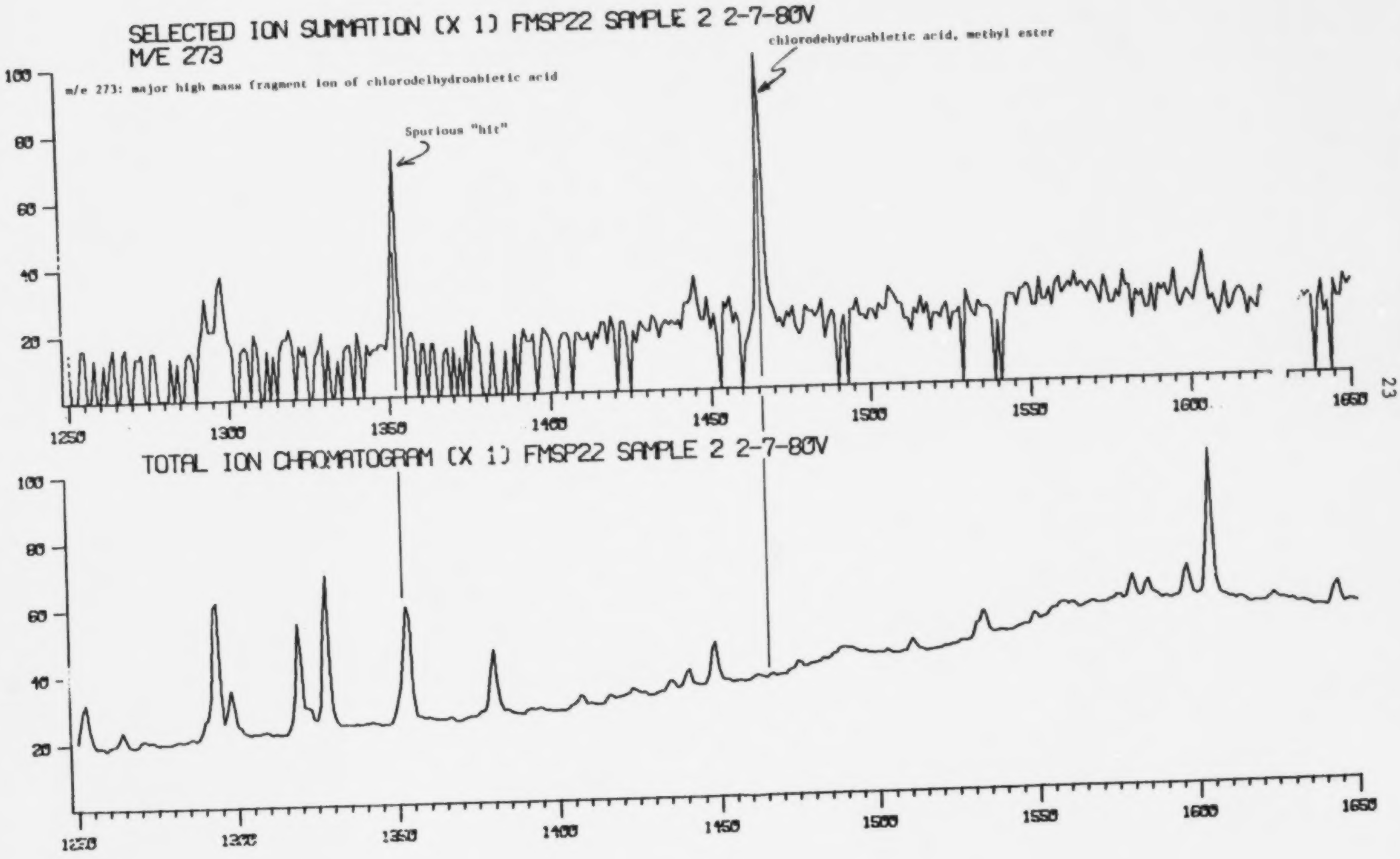


FIGURE 15. EICP CHROMATOGRAM INDICATING THE PRESENCE OF CHLORODEHYDROABIETATE IN THE MARCH 5, 1979 SAMPLE.

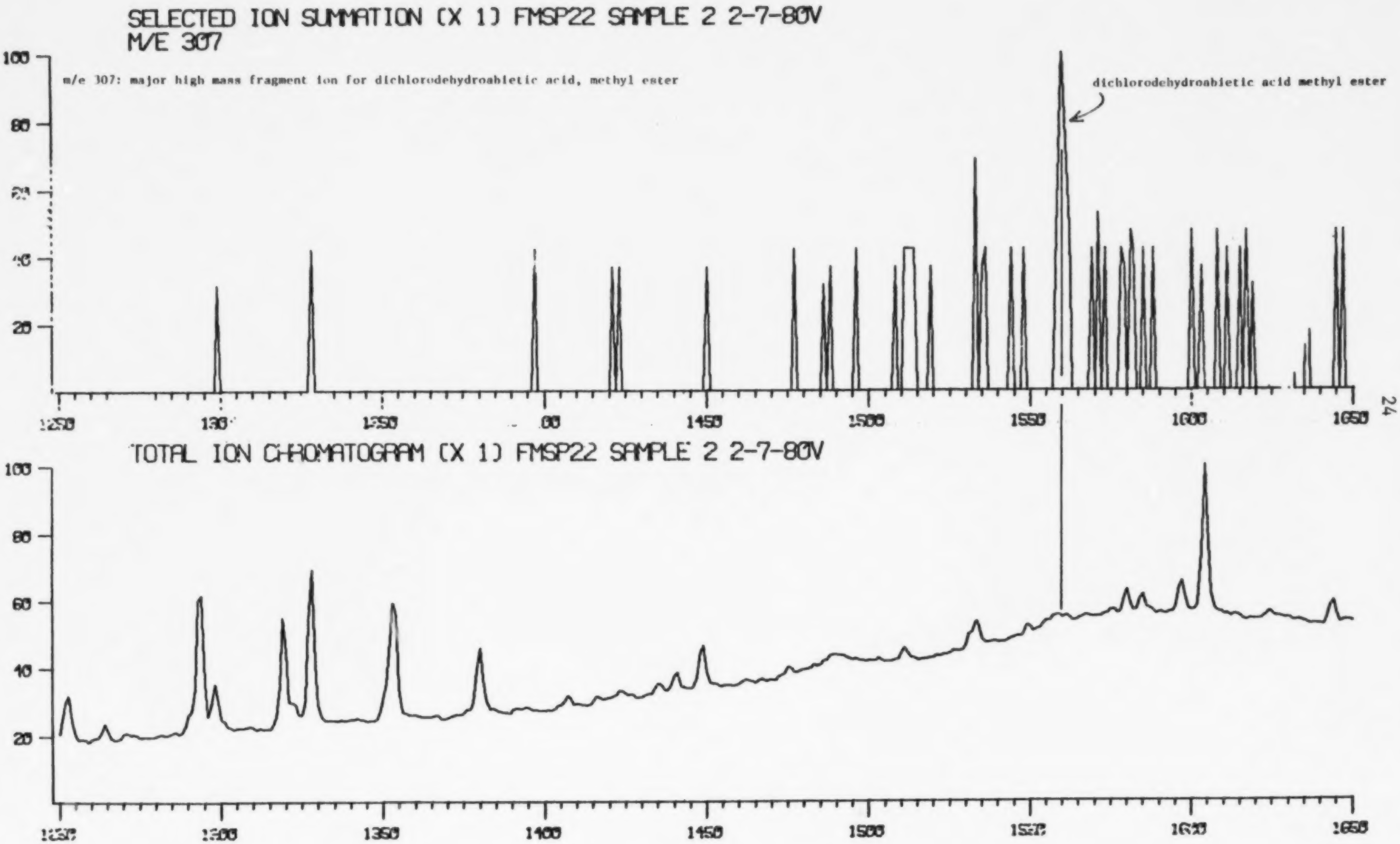


FIGURE 16. EICP CHROMATOGRAM INDICATING THE PRESENCE OF DICHLORODEHYDROABIETATE IN THE MARCH 5, 1979 SAMPLE.

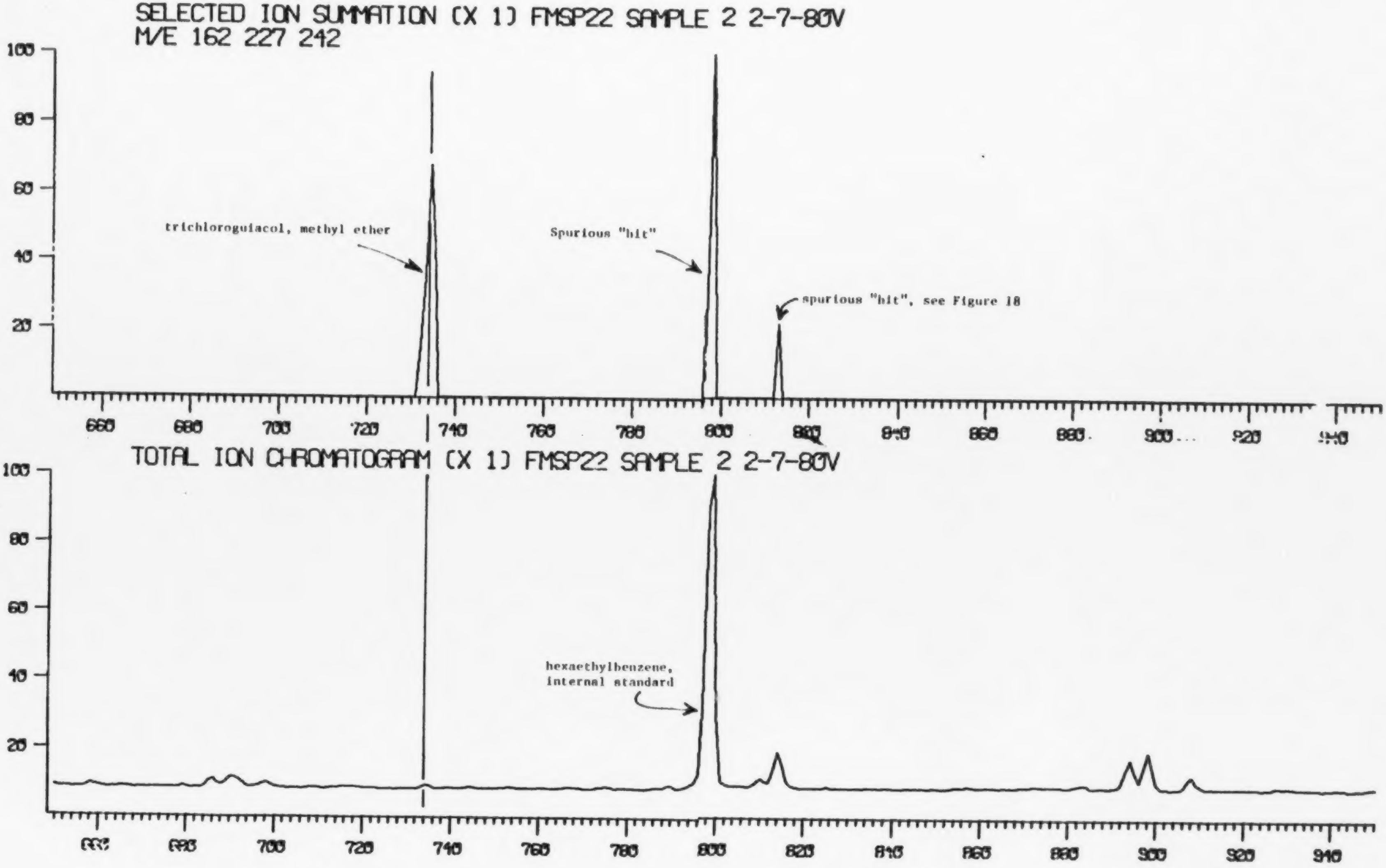


FIGURE 17. EICP CHROMATOGRAM INDICATING THE PRESENCE OF TRICHLOROGUIACOL IN THE MARCH 5, 1979 SAMPLE.

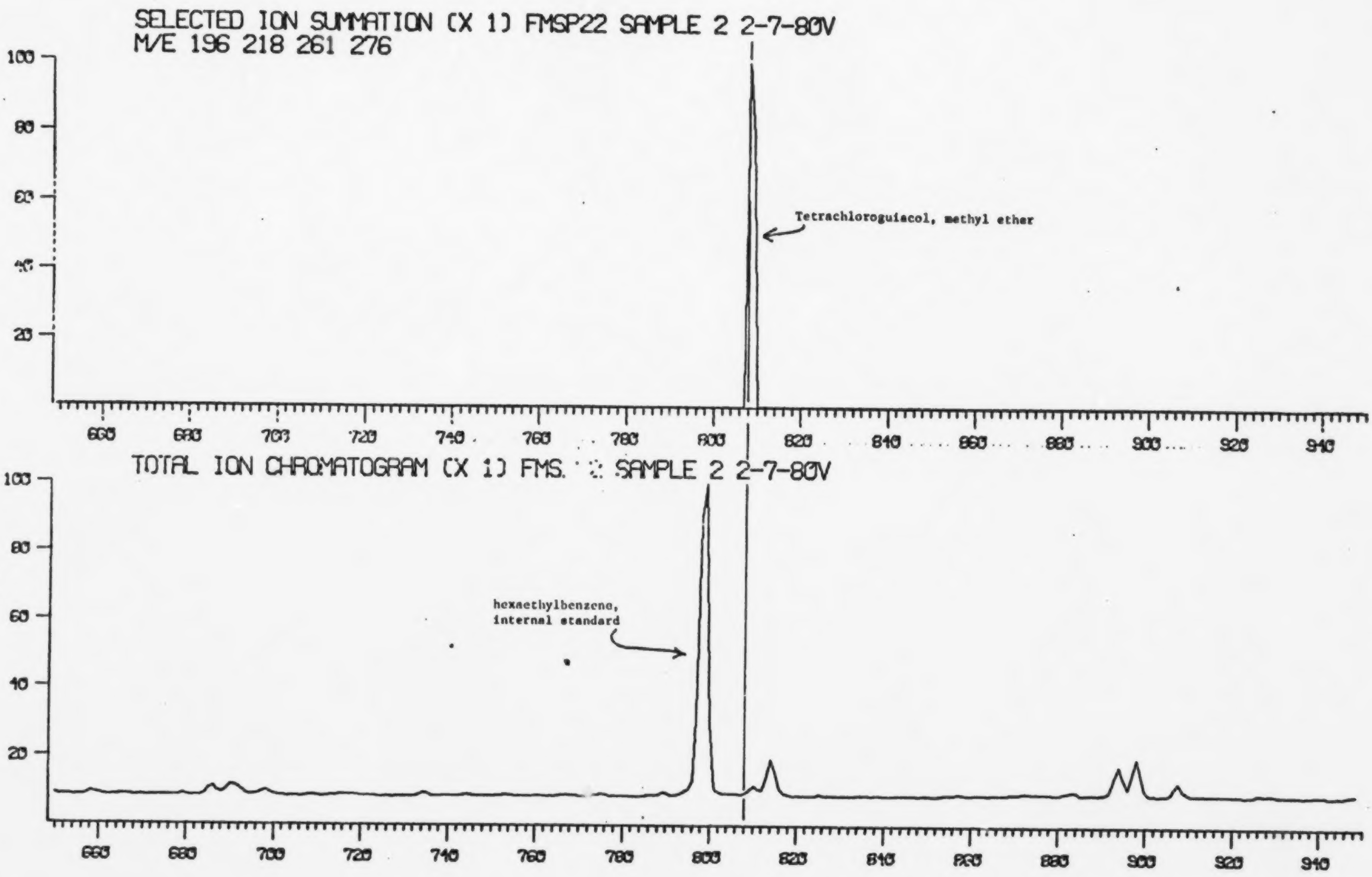


FIGURE 18. EICP CHROMATOGRAM INDICATING THE PRESENCE OF TETRACHLOROGUIACOL IN THE MARCH 5, 1979 SAMPLE.

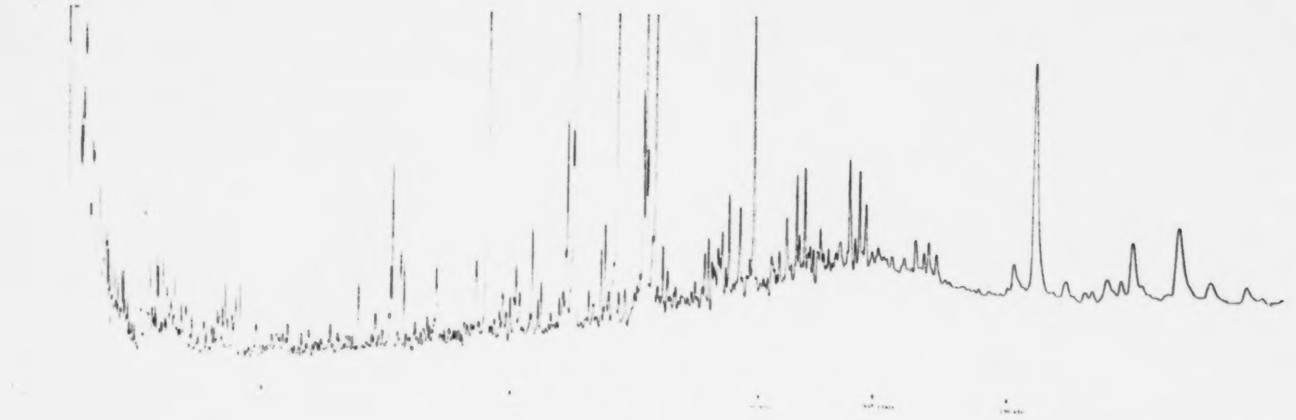


FIGURE 19. $(GC)^2$-FID CHROMATOGRAM OF THE "DAM #2" SAMPLE.

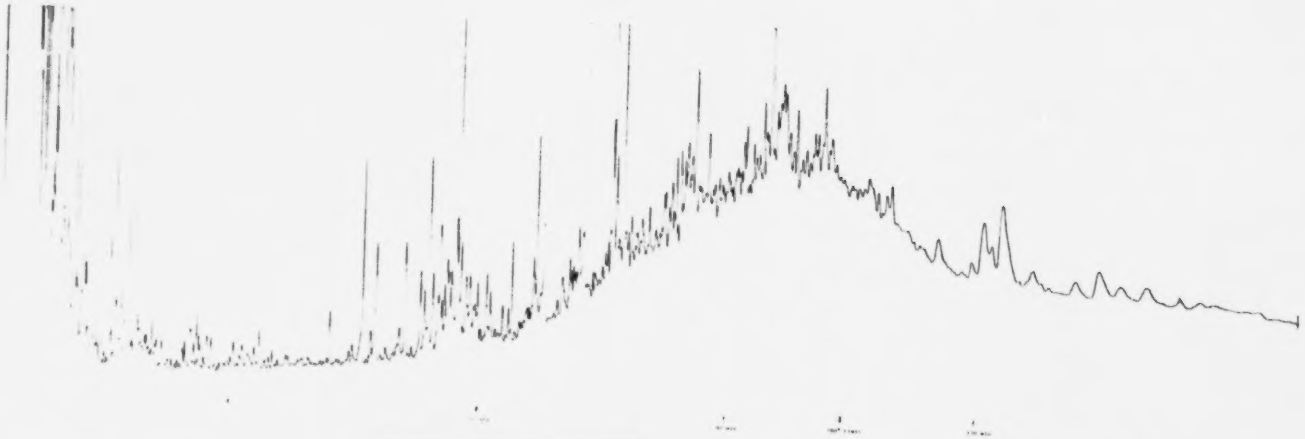


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FIGURE 20. $(GC)^2$-FID CHROMATOGRAM OF THE "DAM #12" SAMPLE.

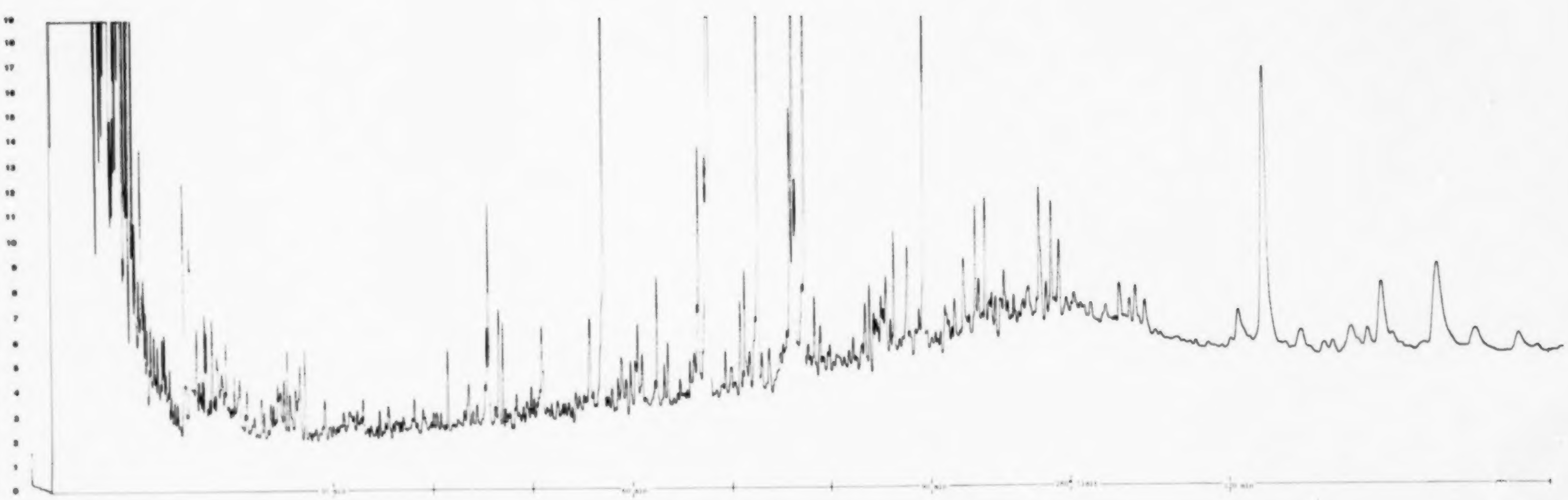
TABLE 3. GC RETENTION DATA FOR RESIN AND FATTY ACIDS AS THEIR METHYL DERIVATIVES

Compound (Free Acid)	RRT(1) (Methyl derivative)
myristic	1.108
palmitic	1.217
steric	1.397
oleic	1.376
linoleic	1.370
abietic	1.620
dehydroabietic	1.584
pimaric(2)	1.501
isopimaric(2)	1.549
monochlorodehydroabietic (isomer A)(2)	1.732
monochlorodehydroabietic (isomer B)(2)	1.758
dichlorodehydroabietic	1.877
trichloroguiacol	0.905
tetrachloroguiacol	1.011

1. RRT = relative retention time; relative to the internal standard, hexaethyl benzene, at 53.533 min.
2. The indicated elution order may be reversed.

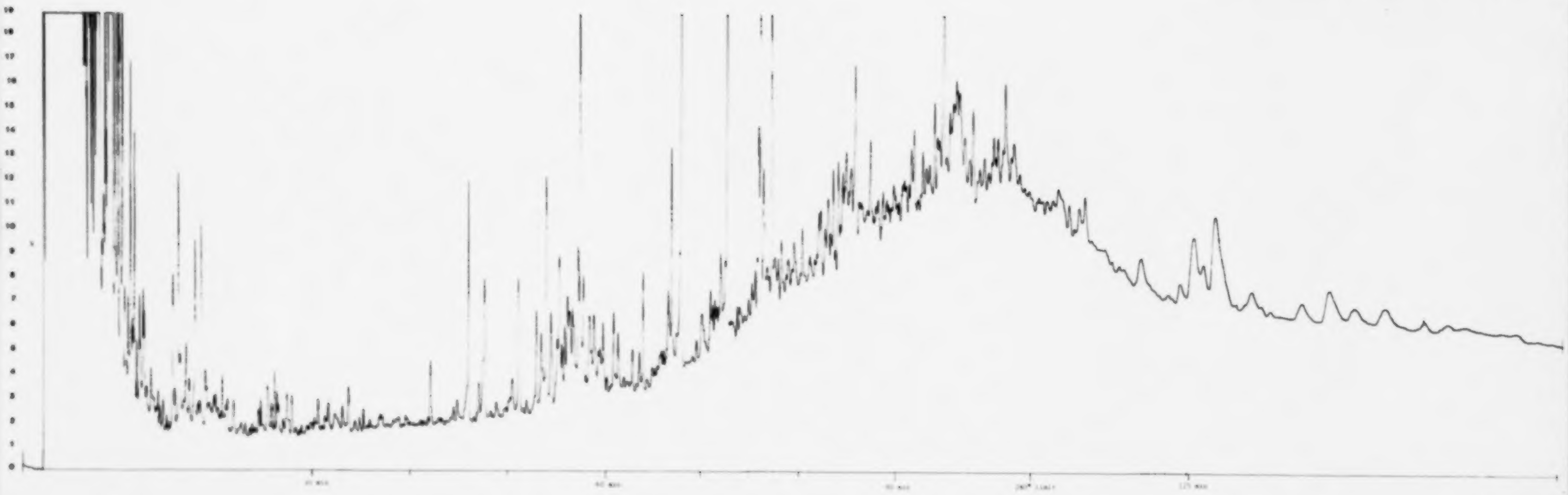
DAM #D-2

SAMPLE LOCATION : ERROL DAM IN ERROL, N.H.



DAM #D-12

SAMPLE LOCATION : DAM ON LITTLE ANDROSCOGGIN RIVER
1/2 MILE UPSTREAM FROM CONFLUENCE
WITH ANDROSCOGGIN RIVER IN AUBURN, MAINE



APPENDIX D

MAINE
DEPARTMENT OF ENVIRONMENTAL PROTECTION
REPORT

STATE OF MAINE
Department of Environmental Protection
MAIN OFFICE: RAY BUILDING, HOSPITAL STREET, AUGUSTA
MAIL ADDRESS: STATE HOUSE, AUGUSTA 04333

Henry E. Warren
COMMISSIONER
289-2811

ADMINISTRATIVE SERVICES:
289-2691

BUREAUS:

AIR QUALITY CONTROL
289-2437

LAND QUALITY CONTROL
289-2111

WATER QUALITY CONTROL
289-2591
OIL POLLUTION CONTROL
289-2591

REGIONAL OFFICES:

31 CENTRAL STREET
BANGOR 04401
947-6746

634 MAIN STREET
PRESQUE ISLE 04769
764-3737

OIL POLLUTION CONTROL
17 COMMERCIAL STREET
PORTLAND
773-6491
OIL SPILL REPORTS ONLY
(TOLL FREE) 1-800-482-0777

CITIZENS' ENVIRONMENTAL ASSISTANCE SERVICE
289-2691
(TOLL FREE) 1-800-452-1942

AIR QUALITY CONTROL
17 COMMERCIAL STREET
PORTLAND
773-0196

LAND QUALITY CONTROL
17 COMMERCIAL STREET
PORTLAND
773-0196

March 28, 1980

William Warren
E. C. Jordan Company
Box 7050, Downtown Station
Portland, Maine 04112

Dear Mr. Warren:

This letter-report is intended to fulfill the Department's obligations to the EPA as outlined in RFQ 79-141 dated December 18, 1978. Because the work performed pursuant to the RFQ is intended to partially support a larger contract between the E. C. Jordan Company and the EPA, it is hereby submitted to the Jordan Company for inclusion in your final report wherever appropriate. It is understood that acknowledgement of authorship will be to the mutual agreement of the Jordan Company and the DEP. A copy of the report is also being submitted to the EPA to facilitate payment of DEP's costs at the earliest opportunity.

INTRODUCTION

The Androscoggin River is culturally impacted during its 175 mile course from Umbagog Lake to its terminus at Merrymeeting Bay in Maine. Several major industries (Brown Paper Company, Boise Cascade Paper Group, International Paper Company, and Pejepscot Paper Company) and municipalities (Rumford/Mexico, Livermore Falls, Lewiston/Auburn, Lisbon Falls, and Brunswick) discharge their treated wastes to the river. Accumulations of river foam in the more populated areas of Brunswick, Lewiston, and Livermore Falls have been the object of public concern and comment for many years. The Department of Environmental Protection contracted with the U. S. Environmental Protection Agency to study the sources and causes of foam including an examination of physical and chemical aspects of the foaming phenomenon. Work was done in consultation and cooperation with the E. C. Jordan Company of Portland, Maine. The ultimate objective of the joint effort will be to recommend methods for reducing the amounts of foam on the Androscoggin River.

RFQ 79-141 established five (5) objectives. More specifically the DEP agreed to attempt to:

1. Characterize the chemical composition of Androscoggin River foam.
2. Identify foam-causing constituents in Androscoggin River foam.
3. Identify the longitudinal distribution of foam-causing constituents in the Androscoggin River water.
4. Identify foam-causing constituents in paper mill effluents to the Androscoggin River.
5. Determine correlations between environmental parameters, foam-causing constituents, and foaming tendency.

This ambitious set of objectives represents perhaps an idealistic approach to understanding a historical problem of foam generation and accumulation on the Androscoggin River. Total accomplishment of all objectives would bring the state-of-the-art much closer to an understanding and possible solution of the foam problem than now exists.

Stated objectives were partially met. Identification of foam-causing agents was the backbone to all objectives. Unfortunately, the composition of foam is extremely complex including anions, cations, resin acids, fatty acids, and nameless other aliphatics, nuclear, and polynuclear aromatics. Due to analytical limitations a complete accounting of all constituents was not possible. Therefore, only partial achievement of the objectives was possible. Our efforts included the following:

1. Observations on the distribution of foam from the headwaters of the Androscoggin River at Errol, New Hampshire to its confluence with the Kennebec River at Merrymeeting Bay. Also included were extended observations at the Route 201 bridge at Brunswick.
2. An examination of resin and fatty acids in foam and water from several point sources and ambient sources of the Androscoggin River as well as a major tributary, the Little Androscoggin River.
3. A mass balance of foam by identification of major organic and inorganic constituents.
4. An examination of the relative foamability of several point sources to the Androscoggin River.

The following report describes in detail the methods and findings of our efforts.

EXPERIMENTAL AND RESULTS

foaming tendency

Foaming tendencies were measured. Despite a review of the literature and several attempts to create an artificial foam generator, none were found entirely suitable for this study. Finally, ASTM method #D3519-76 was chosen. Some modifications were made. A 14 speed Hamilton Beach blender was used at setting #7 for three minutes to generate foam. The height of foam was measured immediately and then again after ten minutes as an estimate of foam persistency. Grab samples of effluent water at Boise Cascade, International Paper Company, Lewiston Treatment Plant, Lisbon Falls Treatment Plant, and Pejepscot Paper Company effluents were collected in October, 1979, and January, 1980, for analysis. Additionally, foamability of point sources mixed at various concentrations with Androscoggin River water from the Virginia Bridge (above Boise Cascade in Rumford) was determined at several temperatures. No adjustments were made for pH or ionic strength.

Several interesting observations can be made. First, foamability appears to be an inverse function of temperature. Both Pejepscot Paper and Boise Cascade effluents created more foam when the temperature decreased from 25°C to 6°C as shown in Table 1. This phenomenon can be explained by the improved hydrophobic bonding by surfactants created at lower temperatures. Secondly, there are considerable differences in foamability and persistence among the point sources. Ranking according to 'head' is Boise Cascade: Lisbon Falls: International Paper: Pejepscot Paper, and Lewiston. The range in 'head' was 25 mm to 5 mm. Also, note that foam persistence (defined as the time for decay to less than 1 mm) was roughly proportional to 'head'; that is, the Boise Cascade and Lisbon Falls effluents persisted far longer (300 sec.) than the Lewiston effluent (30 sec.). Although not necessarily indicative of conditions to be expected in the ambient environment, such comparisons of undiluted effluents may be useful as a 'relative' indicator. In actuality, the combined nominal discharges from the point sources examined amount for approximately 3% of the median discharge (4200 cfs) measured at the USGS Auburn gage.

Longitudinal river foaming tendencies were observed. On June 19, 1979 an aerial reconnaissance was made of the river from Merrymeeting Bay (Brunswick, Maine) to the headwaters at Errol dam (Errol, New Hampshire). Subjective assessment by the writer of foam conditions relating to intensity and persistence were made which are recorded in Table 2. Although subjective observations cannot be easily compared, limited conclusions can be drawn. First, locations of greatest foam intensity and persistence were below Brown Paper, Boise Cascade, Riley Dam, International Paper, Pejepscot Paper, and below the Brunswick Dam. Generally, foam persistence seems to correlate positively with intensity. In no case was there observed both high intensity and persistence above man-made pollution sources, indicating that the foam persistence problem perceived on the lower Androscoggin River is cultural in origin.

Foaming may be related to river flows. An observation point was established at the Route 201 bridge at Brunswick. A cove on the left bank (downstream convention) immediately above the bridge seemed to accumulate river foam and was photographed eleven times from July 6, 1979 to November 28, 1979. All photographs were ranked according to the amount of foam accumulated in the cove and compared to the USGS average daily discharge (Auburn Gage) using Spearman's rank correlation coefficient statistic. For foam against river discharge $r = -0.5$. The relatively large value of r considering the highly subjective means of evaluating foam accumulations in the test cove suggest the strong possibility that the presence of foam on the river is inversely proportional to the river discharge. That is, lower river flows may cause larger amounts of foam by increased surfactant concentration, increased foam generators, or other physical/chemical mechanisms.

mass balance

Foam was collected at several locations. The objective was to chemically characterize foam from major point sources to the Androscoggin as well as ambient foam from non-industrially and industrially impacted locations on the river. Consequently, eight locations were sampled from Brunswick, Maine including locations 10, 11, 16, 21, 22, 25, 28, and 29 described in Table 6 to Errol, New Hampshire. Early in the study, foam samples were collected in a plastic garbage bag. Because of the likelihood of contamination from plasticizers, the technique was modified. Subsequently, foam was collected in a teflon air sampling bag supported in a ten gallon garbage can using a dust pan scoop covered with the same teflon material. The foam was allowed to collapse (typically by settling overnight) and transferred to glass without chemical preservative. Thirty liters of foam yields approximately two liters of liquid.

Samples were analyzed by standard methods. Analysis for solids (suspended, dissolved, and total) were by the usual gravimetric means described in APHA Standard Methods, 14th Edition, 1975. Kjeldahl nitrogen and total phosphorus were determined on Technicon Autoanalyzers using DEP modifications of The Examination of Water and Waste Water, EPA, 1979. Total organic carbon was quantified on a Beckman model 915 analyzer and the metals sodium, potassium, calcium, and magnesium on a Perkin Eliner model 603 atomic adsorption spectrophotometer according to the APHA reference previously cited.

Differences in foam composition are observed. All data on foam composition are listed in Table 3. Three point sources (Brown, Boise, and IP) are considerably higher in sodium than the remaining point source and all ambient locations. The lowest metals were found at the "pristine" Errol dam location followed closely by the Little Androscoggin River. Foam from the three sources noted seems characteristically higher in dissolved solids, total solids, and (in 2 of 3 sources) non-volatile total solids. A causal relationship may exist between high metals and solids. Total organic carbon values are highly variable among all locations with no particular pattern by source. Based on these data, the conclusion might be made that the major difference between point source foam and "pristine" ambient foam can be found not in its organic content but, rather, in the inorganic fraction. An analysis of river water at Topsham for the same parameters is shown in Table 4.

A mass balance of foam was attempted. The total solid residue of foam (dried at 105°C) was considered in two parts: the volatile fraction (at 550°C) and the remaining or non-volatile fraction. The remaining parameters were grouped according to the following assumptions:

A. volatile fraction
    1. total organic carbon
    2. total Kjeldahl nitrogen
B. non-volatile fraction
    1. total phosphorus
    2. sodium
    3. potassium
    4. calcium
    5. magnesium

However, mass balance cannot be attempted without adjusting the stoichiometrics. Total organic carbon (TOC) was assumed to exist as phenols (guaiacol, acetovanillone, syringaldehyde), resin acids, and carbohydrates. Mass to carbon ratios of 1.60, 1.24, and 1.17 respectively were calculated. Furthermore, since phenols, resin acids, and carbohydrates were found in the approximate relative abundance 1:40:40 from the GC/MS analysis described later, an overall mass to carbon ratio of 1.20 was calculated. The ratio was used to calculate the mass of volatile loss from the total organic carbon analysis. Total Kjeldahl nitrogen (amines, proteins, and ammonia) represents an insignificant contribution to the volatile mass (less than one percent) and can probably be ignored. Phosphorus and the remaining metals are assumed to exist in the fired residue as the oxide or a salt. X-ray fluorescence analysis performed on a foam residue by the EPA laboratory, Lexington, Mass., strongly indicates the presence of chlorine and (less strongly) sulfur. Therefore, the mass balance was calculated assuming both oxide and chloride salt form using the following ratios:

	$O^=$	Cl^-
P	2.29	4.44
Na	1.35	2.54
K	1.21	1.91
Ca	1.40	2.80
Mg	1.67	3.96

The mass balance is incomplete. All calculated values are shown in Table 5. The carbon mass accounts for only 30 to 62 percent of the volatile mass. Even an error of 100 percent in the assumed stoichiometric relation (1.20) of mass to organic carbon will not significantly change the recovery. However, a spectrophotometric analysis of river foam from the Topsham Bridge suggests the presence of tannins at about 40 ppm. Since the stoichiometric ratio for tannins to carbon is about 1.91, its inclusion in the carbon mass budget could be significant. Loss of non-carbonaceous materials during firing at 550°C can partially explain the discrepancy. However, acceptance of this hypothesis makes the mass balance of the inorganic (non-volatile) fractions even worse. As it is, neither the oxides nor the chloride salts of analyzed metals can account for the non-volatile mass. Discounting location 10 as an outlier, only 33 to 38 percent of the inorganic mass can be accounted for as the oxide of P, Na, K, Ca, or Mg. Similarly, recovery improves to 65 to 73 percent when the chloride salts are assumed. Either way, there is a significant mass unmeasured in the fraction. The presence of sulfates or sulfonated materials as suggested by x-ray analysis in the residue would have a very major impact on the residue balance. Alternately, a major cation may be present which was not detected by x-ray fluorescence.

GC/MS Analysis

An extensive sampling program was attempted. Twenty four samples of water and/or foam were collected from Errol, New Hampshire to Topsham, Maine from both point sources and ambient sources on the Androscoggin River during the interval 11/2/78 to 6/28/79. Additionally, samples of foam and water were collected from the Little Androscoggin River. Table 6 lists all sources. Water was collected in one gallon dark glass bottles previously washed in pesticide grade dichloromethane or methylene chloride. Foam was collected as previously noted ("mass balance"). All teflon bag surfaces were washed with methylene chloride or dichloromethane and combined with the collapsed foam in glass.

Samples were prepared for analysis. All water and collapsed foam samples were first extracted with dichloromethane. After acidification to pH=2 with sulfuric acid the extraction was repeated. All extracts were combined, dried over Na_2SO_4 and reduced in volume by rotovaporator or Kuderna Danish concentrator. All samples were methylated with diazomethane in the following manner. Diazomethane was prepared by dissolving 2.3 gm of KOH in 2.3 ml of distilled water then adding 25 ml of reagent grade diethylether and cooled to -18°C. In a high draft hood 1.6 gm of N-methyl-N-nitro-Nitrosoquanidine was carefully added to the basic ether. The ether layer was decanted and stored at -18°C in a teflon sealed glass vial. To 0.5 ml of dry extract was added 0.5 ml of reagent grade methanol and 2.0 ml of diazomethane/ether solution. After allowing to stand for 30 minutes, excess diazomethane was removed by stripping with nitrogen gas to a pale yellow color. All analyses performed after 1/31/79 include margaric acid as an internal standard. Recovery studies with oleic acid suggest typical recoveries of 80% can be expected for the system.

Analysis was by GC/MS. A Hewlett Packard model 5992A GC/MS system (extended computer capacity) with membrane separator was used. For analyses dated 1/31/79 and earlier a six foot DEGS-PS (Supelco, Inc.) pack glass column was used; after that date we used splitless injection onto a 40 meter SP2100 (Supelco, Inc.) SCOT glass capillary column. Typical instrument conditions were:

1. Initial Temp: 80°C for 4 min.
2. Program Rate: 4°C/min.
3. Final Temp. 240°C for 45 min.
4. Injection Port: 260°C
5. Carrier gas: 2 ml/min. helium
6. Multiplier: 2200 electron volts

Identification of peaks was by comparing retention times against a standard containing 16 phenols, resin acids, and fatty acids provided by NCASI. Additional confirmation was achieved by comparison of mass spectra. Quantification was based on total ion abundance against margaric acid.

Foam composition is variable. Results are listed in Table 7. Foam from paper mill effluents contained appreciable quantities of resin and fatty acids, but relatively insignificant quantities of phenolic compounds. River foam composition at Topsham appears to be somewhat similar in concentration and distribution of these materials to the paper mill effluents. A notable difference between Topsham River foam and "pristine" foam at Errol, New Hampshire (as well as the less "pristine" Little Androscoggin River) is the absence of resin acids. Their presence may be a partial explanation for the difference in foam persistence previously observed.

GC/MS analysis is incomplete. Typically, only 1 to 20 ppm of mass can be accounted for by analysis for phenolics, resin acids, and fatty acids. In contrast, 100 to 500 ppm should exist based on total organic carbon measurements. Therefore, less than 20% of the organic carbon present in foam appears to exist as a phenolic or resin and fatty acids. As previously noted tannins were detected at approximate 40 ppm in foam from the Topsham site. Furthermore, analysis of foam from the same location by Dr. Daniel W. Armstrong (Georgetown University) has identified 110 ppm of alkyl and aryl sulfates (or sulfonates) by the Methylene Blue reaction and 78 ppm aryl sulfate (or sulfonates) by liquid chromatography. Therefore, there appears to be strong evidence that the organic carbon unaccounted for (more than 80% of the total) may be in the form of tannins and sulfate/sulfonate derivatives or their homologues.

Results of water analysis are in Table 8. Generally, organic concentrations are low or undetectable in ambient waters. Data are insufficient to produce obvious or dramatic conclusions.

CONCLUSIONS:

1. Foam on the lower end of the Androscoggin River is more persistent than the "pristine" end.
2. The amount of foam on the Androscoggin River is inversely proportional to river flow (tentative).
3. Foam generation is inversely proportional to temperature. (tentative)
4. Both inorganic and organic mass balance is incomplete indicating inadequate accountability by the analytical techniques used. Future analysis for tannins (and related substances) plus sulfonated derivatives and sulfates may describe a large portion of the missing materials.

CONCLUSIONS: (cont.)

5. There are substantial differences between paper mill foam and "pristine" foam in the organic to inorganic ratio and in the concentration of resin acids.
6. GC/MS analysis for phenolics, resin acids, and fatty acids accounts for less than 20% of the total organic carbon.
7. A major form of organic carbon may be aryl/alkyl-sulfate/ sulfonates.

The study has been enlightening. No only have we learned more about the chemical composition of foam, but also more about the physical phenomenon. We look forward to studying the subject in more detail.

Yours truly,

Gardner S Hunt

Gardner S. Hunt
Director
Division of Laboratory
and Field Services
Bureau of Water Quality Control
Department of Environmental Protection

GSH/h

Enc.

Sample Source	% Sample Source	Temp. (°C)	Initial Foam Head (mm)	Time for 10 mm Head (sec.)	Time for <1 mm Head (sec.)	Foam Head at 300 sec. (mm)
Boise Cascade	6	6	3	-	2	
	11.3	10	3	-	2	
	16.1	20	10	-	15	
	20.3	25	12	-	23	
	24.2	25	12	-	30	
	27.7	25	15	-	30	
	31.0	25	15	-	40	
	31.0	6	18	-	L240	5
	100.0	6	25	120	L300	
IP	9	6	2	-	3	
	16.5	10	2	-	3	
	22.9	25	10	-	5	
	28.3	25	10	-	5	
	33.1	25	11	-	7	
	37.2	25	13	-	8	
	100.0	6	12	5	90	
Lewiston	2.8	20	j2	-	2	
	5.4	20	j2	-	2	
	8.0	20	j2	-	2	
	10.3	20	j2	-	2	
	12.6	20	j7	-	5	
	14.7	20	j5	-	5	
	17.1	20	j5	-	5	
	100.0	6	5	-	30	
Lisbon Falls	2.3	25	5	-	5	
	4.5	25	5	-	12	
	6.6	25	5	-	15	
	8.4	25	7	-	23	
	100.0	6	25	45	L300	9
Pejepscot Paper	.6	6	k2	-	k1	
	1.2	10	k2	-	k1	
	3.5	25	k5	-		
	10.8	25	j5	-	3	
	10.8	6	12	-	15	
	100.0	6	12	4	60	
Collapsed Foam (below IP)	.4	6	2	-	1	
	.8	10	5	-	3	
	1.2	15	5	-	5	
	2.0	20	7	-	10	
	3.7	25	7	-	60-120	
	5.7	25	10	-	L120	
	7.4	25	12	-	L120	
	16.7	25	16	-	L120	
	100.0	6	30	-	L300	20
Androscoggin River at Virginia Bridge	100.0	6	0	0	0	0

Foamability after 3 min. Blending

Table 1

	Location	Foam Intensity	Foam Persistence
*	Errol Dam (Errol, N. H.)	xx	x
*	Dam above Brown Paper (Berlin, N. H.)	xx	x
*	Brown Paper discharge (Berlin, N. H.)	xxx	x
*	Boise Cascade discharge (Rumford, Maine)	xxx	x
*	Boise Cascade to International Paper	x	x
*	Riley Dam (above IP)	xxx	xx
*	3 dams below IP (Jay, Livermore Falls, Me.)	xxx	xx
*	riffles to Gulf Island Pond (Turner, Me.)	xx	x
*	Gulf Island Pond	x	x
*	outlet Gulf Island Pond	xx	x
*	Great Falls & Bates Canal (Lewiston/Auburn, Me.)	xx	x
*	dam and riffles (Lisbon Falls, Me.)	xx	xx
*	Pejepscot Paper discharge (Topsham, Me.)	xxx	xx
*	Dam (Brunswick, Me.)	xxx	xx

code:	none	x	x
	medium	xx	xx
	intense	xxx	xxx

Brunswick, Me. to Errol, N. H. observations

Table 2

Sample No.	29	28	25	22	21	16	11	10
Total Suspended Solids	440	105	83	230	233	388	170	262(1)
Total Dissolved Solids	430	620	320	290	1610	960(1)	1050	410
(volatile diss. sol.)	280	240	191	170	960	330	546	160
(non-volatile diss. sol.)	150	380	129	120	650	630	504	250
Total Solids	940	674	421	510	1538	1484	1780	367
(volatile tot. sol)	730	394	333	-	572	640	1114	296
(non-volatile tot. sol)	210	280	88	-	966	844	666	71
Total organic carbon	380	166(2)	83(2)	260	177(2)	262(2)	450(2)	138(2)
Total Kjeldahl nitrogen	5.0	-	-	3.6	-	-	-	-
Total phosphorus	2.0	3.5	1.7	0.7	0.7	0.8	2.1	1.0
Sodium	22	24	12	25	220	170	150	1.3
Potassium	3.1	16	1.8	1.8	11	8.8	9.0	0.7
Calcium	20.	22	7.3	10.6	30	33	21	2.6
Magnesium	2.4	5.8	0.85	1.3	2.1	2.1	1.8	0.58

(1) ave. of duplicate analyses

(2) estimate due to extended holding time

Analysis of Collapsed Foam (ppm)

Table 3

Sample No.	29
Sample Date	11/20/78
Total Suspended Solids	4.3
Total Dissolved Solids	120
(Volatile Diss. Sol.)	26
(Non-volatile Diss. Sol.)	94
Total Solids	125
(Volatile Tot. Sol.)	31
(Non-volatile Tot. Sol.)	94
Total Organic Carbon	11
Total Kjeldahl Nitrogen	0.6
Total Phosphorus	0.09
Sodium	17
Potassium	1.6
Calcium	6.4
Magnesium	1.1

Analysis of River Water (ppm)

Table 4

Sample No.	29			28			25			22			21			16			11			10		
T. volatile residue	730			394			333			-			572			640			1114			296		
mass factor		1.20			1.20			1.20			1.20			1.20			1.20			1.20			1.20	
(TOC)	-	456		-	199		-	100		-	312		-	212		-	314		-	540		-	166	
(TKN)	-			-			-			-			-			-			-			-		
(subtotal)	730	456		394	199		333	100		-	312		572	212		640	314		1114	540		296	166	
(% residue)	-	62		-	51		-	30		-			-	37		-	49		-	48		-	56	
T. non. vol. residue	210	-	-	280	-	-	88	-	-	-	-	-	966	-	-	844	-	-	666	-	-	71	-	-
Anion assumed	-	O⁼	Cl⁻	-	O⁼	Cl⁻	-	O⁼	Cl⁻		O⁼	Cl⁻	-	O⁼	Cl⁻	-	O⁼	Cl⁻	-	O⁼	Cl⁻	-	O⁼	Cl⁻
(F)	-	4.6	8.9	-	8.0	15.5	-	3.9	7.5	-	1.6	3.1	-	1.6	3.1	-	1.8	3.6	-	4.8	9.3	-	2.2	4.4
(Na)	-	30	56	-	32	61	-	16	30	-	34	64	-	297	559	-	230	431	-	203	381	-	1.8	3.3
(K)	-	3.8	5.9		19	31	-	2.2	3.4	-	2.2	3.6	-	13	21	-	11	17	-	11	17	-	.8	1.3
(Ca)	-	28	56		31	62	-	10	20	-	15	30	-	62	86	-	46	92	-	29	59	-	3.6	7.3
(Mg)	-	4.0	9.5		9.7	23	-	1.4	3.4	-	2.2	5.1	-	3.5	8.3	-	3.5	8.3	-	3.0	7.1	-	1.0	2.3
(subtotal)	210	70	136	280	100	193	88	34	64	-	55	106	966	357	675	844	292	552	666	250	473	71	9.4	19
(% residue)	-	33	65	-	36	69	-	38	73	-	-	-	-	37	70	-	35	65	-	38	71	-	13	27
T. residue	940	-	-	674	-	-	421	-	-	510	-	-	1538	-	-	1484	-	-	1780	-	-	367	-	-
(total)	940	526	592	674	299	392	421	136	164	510	367	418	1538	569	887	1484	606	866	1780	791	1013	367	175	185
(% T. residue)	-	56	63	-	44	58	-	32	39	-	72	82	-	37	58	-	41	58	-	44	57	-	47	50

Foam Residue Mass Balances (ppm or percent)

Table 5

Errol Dam - Errol, N. H.	6/28/79	F, W	10
Brown Paper Co. eff. - Berlin, N.H.	6/28/79	F, W	11
Virginia Br., Rumford, Me.	3/15/79	W	12
	6/28/79	W	13
Boise Cascade effluent - Rumford, Me.	1/31/79	F, W	14
	2/21/79	F, W	15
	6/28/79	F	16
1 mi. below Boise Cascade effluent	3/15/79	W	17
4 mi. above International Paper	3/15/79	W	18
	6/28/79	W	19
International Paper eff. - Jay, Me.	2/21/79	F, W	20
	6/28/79	F, W	21
Dam below International Paper eff.	11/2/78	F, W	22
	3/15/79	W	23
	6/28/79	W	24
Dam, Little Androscoggin R.-Auburn, Me.	6/28/79	F, W	25
Below Gypsum Mill-Lisbon Falls, Me.	6/28/79	W	26
Pejepscot Paper eff. - Topsham, Me.	3/15/79	F, W	27
	6/28/79	F, W	28
Foot Br. or Rt. 201 Br.-Topsham, Me.	11/20/78	F, W	29
	12/21/78	F	30
	1/29/79	F	31
	3/5/79	F, W	32
	6/28/79	F, W	33

Sampling for Foam & Water GC/MS Analysis

Table 6

Sample No.		10	11	14	15	16	20	21	22	25	27	28	30	31	32	33
Phenolics	Total	K	230	K	K	510	K	302	K	K	K	K	K	K	100	K
2, 4 Dichlorophenol		K	K	K	K	K	K	K	K	K	K	K	K	K	K	K
2, 4, 6 Trichlorophenol		K	K	K	K	K	K	K	K	K	K	K	K	K	K	K
Pentachlorophenol		K	K	K	K	K	K	K	K	K	K	K	K	K	K	K
Trichloroguaiacol		K	110	K	K	300	K	180	K	K	K	K	K	K	K	K
Tetrachloroguaiacol		K	120	K	K	210	K	122	K	K	K	K	K	K	100	K
Pentachloroguaiacol		K	K	K	K	K	K	K	K	K	K	K	K	K	K	K
Resin Acids	Total	0	540	16137	3664	6840	2144	1932	1234	K	456	1015	1276	5095	2523	400
Sandaracopimaric acid		K	K	K	K	K	K	K	K	K	K	K	K	K	K	K
Pimaric acid		K	K	2865	432	690	539	415	K	K	K	70	K	1064	467	100
Abietic acid		K	350	3202	1261	2250	843	280	877	K	K	375	355	K	849	165
Dehydroabietic acid		K	190	1030	640	795	762	625	357	K	456	165	493	1943	950	135
Monochlorodehydroabietic acid		K	K	K	K	K	K	K	K	K	K	K	K	K	K	K
Isopimaric acid		K	K	9040	1331	3105	K	612	K	K	K	405	428	2088	257	K
Fatty Acids	Total	1349	1444	2854	5568	5520	2511	1089	446	1116	625	1835	938	11979	3072	618
Linoleic acid		90	235	835	665	1040	762	K	72	K	307	450	K	2039	408	100
Linolenic acid		K	610	700	3300	3450	K	365	K	K	K	K	K	K	617	K
Oleic Acid		220	237	K	385	K	368	K	100	277	K	245	375	5027	940	118
9, 10 Dichlorostearic acid		K	K	K	665	K	581	K	K	K	K	K	K	K	K	K
Stearic acid		270	190	955	221	430	400	K	200	K	200	15	450	3150	312	200
Palmitic acid		602	172	364	332	405	400	290	74	587	118	150	113	1763	795	165
Myristic acid		167	K	K	K	195	K	132	K	252	K	975	K	K	K	35
	Grand Total	1349	2214	18991	9232	12870	4655	3021	1680	1116	1081	2850	2214	17074	5695	1018

Note: K = less than 1 ppb

GC/MS Analysis of Foam (ppb)

Table 7

Sample No.	10	11	12	13	14	15	17	18	19	20	21	22	23	24	25	26	27	28	29	32	33
Phenolics Total	K	K	K	K	K	K	K	K	K	28	36	K	K	K	K	K	K	K	K	K	K
2, 4 Dichlorophenol	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K
2, 4, 6 Trichlorophenol	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K
Pentachlorophenol	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K
Trichloroguaiacol	K	K	K	K	K	K	K	K	K	16	23	K	K	K	K	K	K	K	K	K	K
Tetrachloroguaiacol	K	K	K	K	K	K	K	K	K	12	13	K	K	K	K	K	K	K	K	K	K
Pentachloroguaiacol	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K
Resin Acids Total	K	34	K	2	382	377	34	15	451	484	46	K	30	37	K	K	199	3.5	K	46	K
Sandaracopimaric acid	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K
Pimaric acid	K	K	K	K	K	37	K	K	515	45	26	K	K	7	K	K	K	K	K	4	K
Abietic acid	K	18	K	2	126	125	14	15	14	125	20	K	15	13	K	K	80	3.5	K	18	K
Dehydroabietic acid	K	16	K	K	71	120	20	K	12	157	K	K	15	17	K	K	119	K	K	24	K
Monochlorodehydroabietic acid	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K
Isopimaric acid	K	K	K	K	185	95	K	K	K	157	K	K	K	K	K	K	K	K	K	22	K
Fatty Acids Total	K	52	K	12	671	708	42	37	195	578	88	K	65	37	315	24	75	22	K	22	K
Linoleic acid	K	K	K	K	100	40	6	K	21	31	K	K	[illegible]	K	K	K	K	4	K	4.3	K
Linolenic acid	K	K	K	K	88	K	K	K	K	195	K	K	K	K	K	K	K	K	K	K	K
Oleic acid	K	K	K	K	85	59	K	K	45	57	25	K	5	K	K	K	K	10	K	12	K
9, 10 Dichlorostearic acid	K	K	K	K	K	182	K	K	K	180	K	K	22.5	K	K	K	K	K	K	K	K
Stearic acid	K	26	K	3	314	187	15	22	39	25	21	K	17.5	15	K	13	75	K	K	K	K
Palmitic acid	K	26	K	7	84	27.5	15	15	70	90	42	K	15	16	315	11	K	8	K	6.3	K
Myristic acid	K	K	K	2.2	K	212	6	K	20	K	K	K	K	6	K	K	K	K	K	K	K
Grand Total	K	86	K	15	1050	1085	76	73	736	1090	170	K	95	74	315	24	274	26	K	91	K

Note: K = less than 1 ppb

GC/MS Analysis of Water (ppb)

Table 8

EPA	Environmental Protection Agency
RFQ	Request for Quotation
DEP	Department of Environmental Protection
ASTM	American Society of Testing Methods
USGS	United States Geological Survey
r	Spearman Rank Correlation coefficient
APHA	American Public Health Association
TOC	Total Organic Carbon
SCOT	Support coated open tubular
ppm	parts per million (milligrams per liter)
mm	millimeter
^{o}C	degrees centigrade (celsius)
L	greater than
j	approximate
K	less than
IP	International Paper
BC	Boise Cascade Paper Group
BP	Brown Paper Company
PP	Pejepscot Paper Company
GC/MS	gas chromatography/mass spectrometry

Abbreviations Used

Table 9